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THE CHEMICAL TREATMENT OF TRINIDAD DRILLING FLUID.*

By I. McCallum, B.Sc. (Assoc. Member).

Synopsis.

Apart from density, the three physical characteristics of drilling fluid which are of paramount importance in assessing its value in practice are viscosity, gel strength and its ability to form a mud sheath. For the experiments described two basic forest clay muds of 80 and 85 lb. per cu. ft. loaded with barytes to 110 lb. per cu. ft. were used, and the relative effect on viscosity and gel strength of sodium silicate solution and quebracho/caustic soda solution was investigated. Not only was the quebracho solution shown to be superior in reducing the viscosity of the mud, but it was also found that considerable over-dosage of quebracho can take place without the mud acquiring a high gelling rate. The silicate-treated muds, on the other hand, rapidly developed dangerously high gel strengths once the optimum point had been passed. Experiments were also carried out to investigate the gelling effect produced by cements in drilling fluid, and methods of overcoming this effect. It was shown that cement had the power of cancelling the viscosity-reducing properties of silicate, whilst quebracho successfully lowered the viscosity to its normal value. Two other chemicals, sodium tannate and sodium gallate, were found to be, if anything, better than the quebracho in this respect, but in the absence of cements their action was considerably less.

The theoretical aspects of the question are briefly dealt with.

Introduction.

The chemical treatment of drilling fluid is a subject which has frequently been discussed in the technical literature, but always with the realization that any results arrived at cannot be of general interest from the quantitative point of view. The clays and other materials used in the preparation of drilling fluid vary widely in properties, such as chemical analysis, colloidal content, ionizable matter, etc. A full knowledge of all the factors involved would be very difficult of attainment, but would fully justifiy the research involved; the varying properties of mud with chemical treatment would then be to some extent predictable.

The following considerations are therefore primarily concerned with conditions existing in Trinidad. The experiments described serve to indicate the scope and utility of the chemicals found to be of greatest use in reducing mud viscosities.

The basic drilling mud is formed naturally in the course of penetrating a series of highly colloidal marine clays. The Forest and Intermediate Clays are typical of these beds. This fluid has excellent properties, is quite stable in the densities used and shows no signs of sedimentation when the weight is in excess of 65–67 lb. per cu. ft. In order to maintain the necessary

* Paper read at a General Meeting of the Trinidad Branch held at the Apex Club, Fyzabad, on March 31st, 1937, Mr. G. H. Scott, B.Sc., in the Chair.

hydrostatic pressure on the oil and gas formations, mud weights of from 90–130 lb. per cu. ft. are required. The clay mud in excess of 80 lb. per cu. ft. shows a sharp rise in viscosity, together with rapid gelling. Barytes and water are added to further increase the weight when necessary, and in order to maintain this in a good pumpable condition, and to offset the effect of the continual incorporation of fresh clay from cuttings, the addition of viscosity-reducing chemical becomes necessary. A normal barytes laden mud over about 110 lb. would be quite unworkable in the absence of chemical if the barytes content were kept down to economic limits. The approximate upper limit of 130 lb. mentioned corresponds to a solid concentration in the neighbourhood of 75 per cent. by weight dependent on the barytes/clay ratio. Preserving such a mud in a pumpable condition without undue barytes consumption is a matter of considerable financial importance.

Laboratory Examination of Mud.

The samples of mud used in the following experiments were prepared in the laboratory. It was not found practicable in general to use shale mud drawn from drilling wells, owing to such fluid being of lower density than the ultimate shale base in the barytes mud later in use. Very little has been mentioned in the literature with regard to the method of preparation of samples. This, however, has been found to be a matter of considerable importance in order that consistent results may be obtained.

For instance, in the course of examining the viscosity characteristics of a series of local clays, fine grinding of the dried sample was resorted to (150 mesh), followed by agitation with water in the required proportions. Remarkably low viscosities were found on the resultant mud. However, after 2–3 days the fluid thickened, indicating that further slow sub-division of the clay was taking place.

The method finally adopted consisted in soaking the samples in water for 1–2 days, during which time satisfactory disintegration took place, due to water absorption. The saturated clays and water were then agitated, and finally squeezed through a 40-mesh sieve. It would, no doubt, be preferable to use a finer sieve, but with the heavy muds handled this is not always practicable. Samples so prepared were found to be consistent and constant in properties. Fresh cores of the Forest Clay were used generally for the preparation of the basic clay mud. It is essential that such shale should be fresh, for it has been found that cores which had lost a large percentage of their connate water and had become oxidized, gave abnormally low viscosity muds.

Physical Properties.

Apart from the density, there are three physical characteristics of drilling fluid which are of paramount importance in assessing its value in practice. All three are intimately connected with the method of chemical treatment. They are :—

(*a*) Viscosity.
(*b*) Gel strength and its rate of increase with time.
(*c*) Mud-sheath building properties.

Viscosity.

It is a recognized fact that mud viscosities as measured in the usual orifice viscometer can give somewhat indeterminate results, dependent on previous mechanical history of the fluid tendency to gel and rate of shear in the instrument. In so far as viscosity is concerned with the pumpability of a mud at a drilling well, it is therefore only logical that measurements should be carried out in such a manner as to reflect field conditions as closely as possible. Various writers have commented on these phases of mud viscosity. Andrews[1] distinguishes three types of linear flow with thixotropic liquids passing through capillaries.

(*a*) Ordinary stream line flow.
(*b*) A gel core surrounded by a sol film.
(*c*) A gel core surrounded by a water film, the latter existing under conditions of rapid gelling.

Clearly any results obtained under the two latter conditions would be of little use in arriving at frictional resistance in the drilling well-mud system. As a result, many workers have abandoned the use of orifice viscometers, and have adopted rotational instruments of the type of the Stormer and MacMichael, which are capable of supplying results at varying rates of shear.

In the following experiments an orifice viscometer was used, and the size of the orifice varied in order to reduce to a minimum the tendency to gel during the time of flow. In most cases, under optimum conditions of chemical treatment, the fluid behaved as a true liquid and this factor was of no importance whatever.

The results were expressed in terms of kinematic viscosity, and in order to make these figures more readily understandable, Fig. 6 is given, in which the relationship between kinematic viscosity and time in seconds on the Trinidad I.P.T. viscometer as used on the rigs is shown. It was not considered advisable to use the latter unit directly on the viscosity curves, firstly because it is of only local interest, and secondly below 20 seconds time of flow in the local instrument turbulent flow sets in, and consequently the figures no longer give a true picture of the viscosity. This viscometer consists of a cylindrical vessel 12 in. high by 8 in. diameter, carrying on the under-side a vertical capillary 3 in. long by $\frac{7}{32}$ in. diameter. The vessel is filled with mud, and the time of efflux of 750 c.c. recorded as the viscosity.

Generally speaking, a properly conditioned mud in practice shows a viscosity of 20–25 seconds at 95 lb. and 50–60 seconds at 115 lb.

Gel Strength.

Gel strength, or shear force and yield point, as it has been called elsewhere, is, like viscosity, a function of the internal structural and frictional forces of the fluid. The two properties are necessarily interdependent to some extent, but the separate measurements are essential, because they serve to characterize the mud under two different conditions—namely, at rest and in motion. A single gel-strength measurement indicates very little, but when this quantity is measured at successive intervals of time, it tells one what is happening to a stationary column of mud in a well left standing over

a period of time. As pointed out by Meyer,[2] it is of very great importance to obtain low-gel-strength muds, to facilitate the running of the Schlumberger electrical coring apparatus. Similarly, other operations, such as running casing and withdrawing drill-pipe, call for muds of low gel strength.

A certain minimum gel strength is, of course, necessary to inhibit settling of the mud constituents. This, however, is always present, and the problem is solely one of avoiding the undesirable features attendant on the value becoming too high.

It has been found that a rough proportionality exists between this property, measured immediately after agitation, and viscosity. For this reason it has been the practice to rely mainly on a series of gel-strength tests in any mud experiments carried out.

Meyer describes a shearometer made of a strip of metal. This is open to the objection that it is limited at the lower end of the scale by the high density of the metal. The author prefers to use a calibrated hollow glass rod which will float in water about three-quarters submerged, and at successively lower points for the heavier drilling fluids. The mud samples are handled in 100-c.c. cylinders. The rod is lowered gently into the mud and allowed to sink to a position of equilibrium. A flanged metal tube resting on top of the cylinder maintains the rod in a vertical position. The gel strength is then readily calculated from the difference between the theoretical floating point and the actual point to which penetration takes place.

Such a test is simple, rapid and certainly more informative than a viscosity determination when carried out over successive periods of time.

Mud-Sheath Building Properties.

The power to build up a thin, impervious sheath on the walls of a drilling well is one of the recognized features of a good drilling fluid.

Frequent instances of lost circulation through thief sands or fissures have been encountered. The mud properties which have any bearing on this subject will merit investigation.

In general, it can be said that a minimum gel strength is necessary. On the other hand, too high a gel strength will result in additional pressure being placed on the formation for the same weight of mud, thus enhancing breakdown of the mud sheath. Again, the weighting of mud with barytes or coarse clays tends to induce porosity of the sheath, and increase its thickness to such a point that it is liable to impede drilling and also to be readily broken away.

EXPERIMENTAL WORK.

Use of Sodium Silicate and Quebracho.

Until quite recent times sodium silicate was the generally accepted viscosity-reducing chemical used in Trinidad. Results were not uniformly satisfactory, and within the last year quebracho, in conjunction with other chemicals, has taken its place, and has been shown to give considerably better service.

Figs. 1, 2, 3 and 4 show comparative tests on the two chemicals. In order to indicate the effect of shale concentration, two basic forest clay

SODIUM SILICATE TESTS

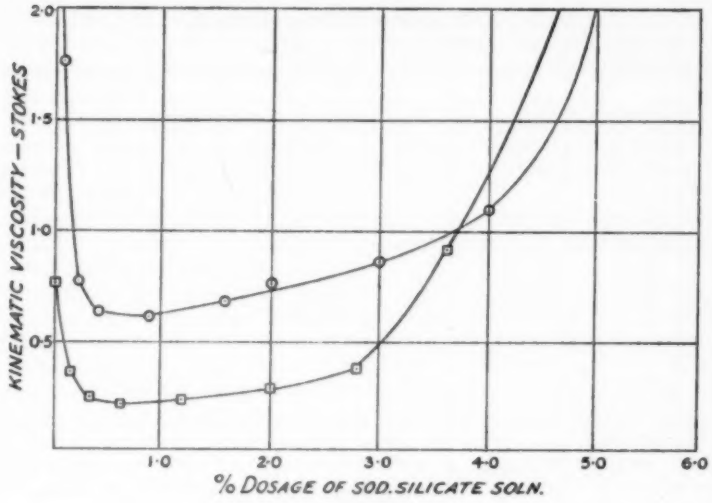


FIG. 1.

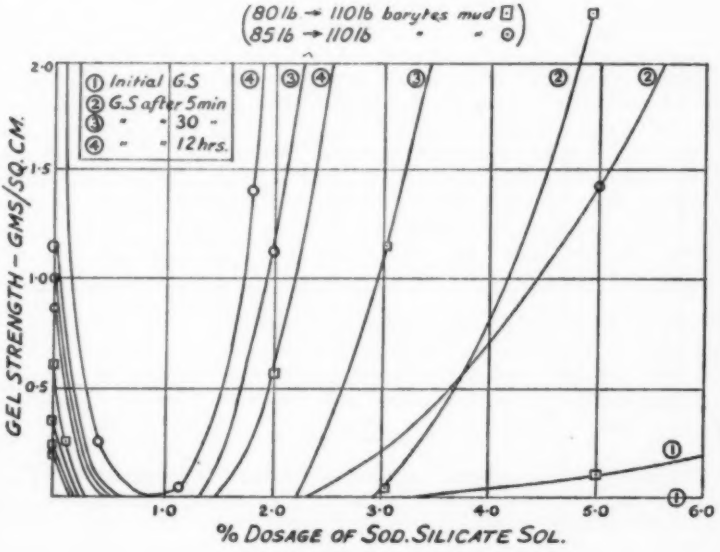


FIG. 2.

QUEBRACHO / N_AOH TESTS

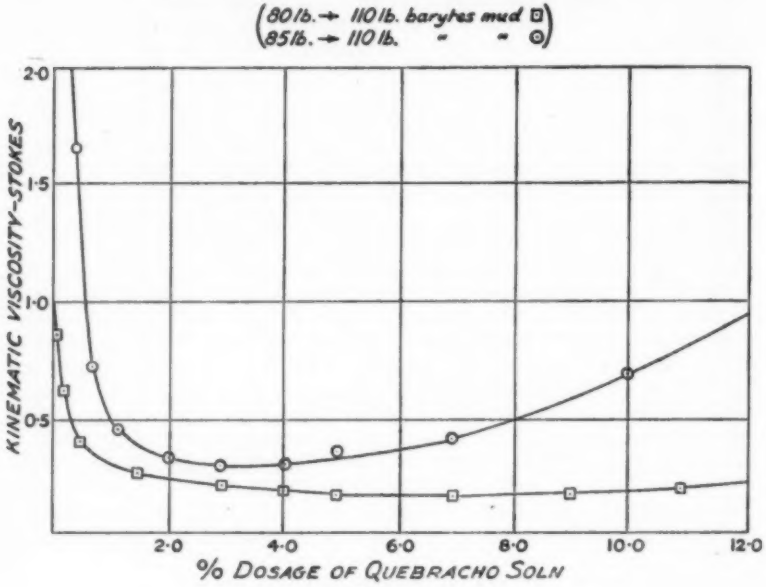


FIG. 3.

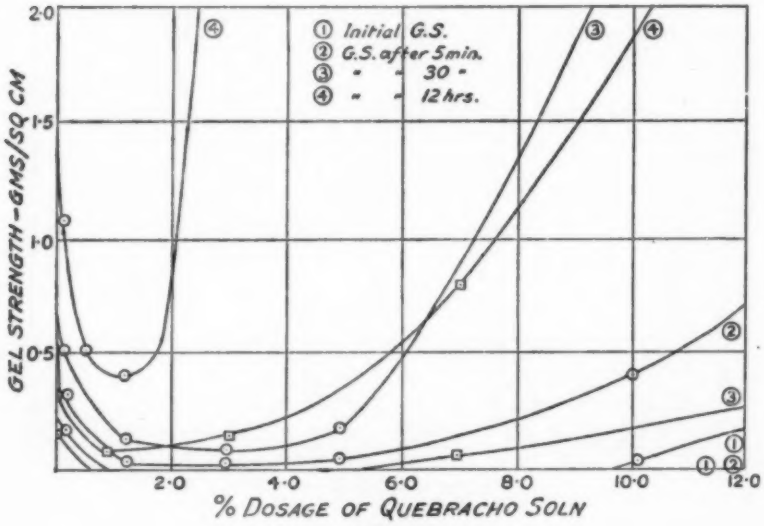


FIG. 4.

muds were prepared of 80 and 85 lb. per cu. ft. in weight. These were loaded with barytes to 110 lb. per cu. ft. to furnish the fluids for the viscosity and gel-strength experiments.

The sodium silicate solution used consisted of water-glass diluted with its own volume of water. The quebracho solution was prepared by dissolving 10 gm. of quebracho and 10 gm. of caustic soda in water and making up to 100 c.c.

It will be noted, on consulting the figs. referred to, that a number of the curves are apparently extrapolated. In order to make the diagrams compact, the higher readings of viscosity and gel strength lying on these curves were omitted.

Since the comparison of the two chemicals rests to some extent on costs, it should be mentioned that the silicate solution has a 50 per cent. greater value than the quebracho solution.

Considering first of all the viscosity curves, it is seen that silicate gives a minimum viscosity in the neighbourhood of 0·6 per cent. with both muds. With the quebracho mud tests, however, the minimum appears at 3 per cent. for the 85-lb. to 110-lb. mud, and about 6 per cent. for the 80-lb. to 110-lb mud. In the latter case, however, the drop in viscosity from a 2 per cent. dosage is so slight that any further addition of chemical is in actual practice unnecessary. Silicate added in excess of 3 per cent. leads to a very sharp rise in viscosity, and over 5–6 per cent. almost instantaneous solidification of the mud takes place. Quebracho-treated muds, on the other hand, show a far more gradual rise after the minimum, and no sharp increase of viscosity is apparent until the dosage reaches 15 per cent. Comparing the effect of chemical on the two different muds used, it is seen that quebracho is able to cope with increased clay content in a far more satisfactory manner than silicate, the ratio of the minimum viscosities being 1 to 1½ and 1 to 3 respectively.

Referring now to the curves on figs. 2 and 4, which show the gel strengths developed after various periods of time, it is immediately evident that the silicate-treated muds rapidly developed dangerously high values once the optimum point has been passed, whereas considerable over-dosage of quebracho can take place without the mud acquiring a high gelling rate. With regard to curve (4) in Fig. 4, it should be mentioned that the quebracho had, in the higher dosages, become concentrated towards the upper part of the cylinder after 12 hours. It is difficult to understand why this should take place, but it had, of course, the effect of giving abnormally high readings.

Briefly it can be said that the quebracho solution is the superior chemical because, firstly, it is more able to cope with increase in clay content, and secondly, considerable over-dosage can take place without any injurious results.

Other Chemicals.

The use of various other chemicals has been mentioned from time to time in the literature. Fig. 5 sets forth a few gel-strength dosage curves. It will be noted that sodium hydroxide has no appreciable thinning properties used in conjunction with local mud ; on the contrary, considerable thickening takes place.

Action of Cement on Drilling Fluid.

It is a well-known fact that mud contaminated with cement in the process of cementing a string of casing can become very thick and unworkable. A series of experiments which were carried out throw some light on this matter, and this work has afforded some very useful information on the whole subject of the chemical treatment of muds. Hydrated cement to the extent of 1–2 per cent. was found to be equally as effective as neat cement in producing thick muds. Evidently the cement contained ionizable material which was responsible for the gelling effect. Hydrated cement was exhaustively extracted with water, and the residue was found

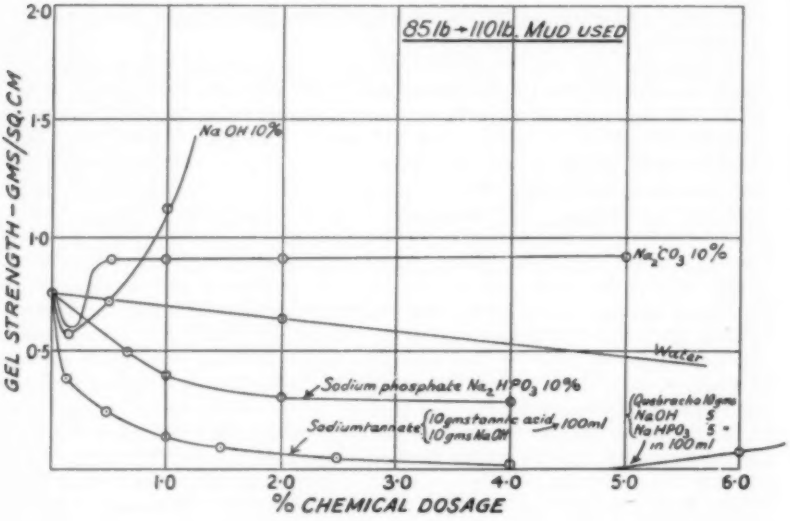


FIG. 5.

to be completely inert towards mud. The extract was analysed, and found to consist mainly of calcium hydroxide, together with small quantities of alumina and calcium sulphate. Solutions of these chemicals were prepared, and found to give results similar to those found with the cement itself. Clearly the calcium ion was responsible for the gelling, and this was found to be the case regardless of the nature of the acid radical.

Further experiments were carried out, aimed at finding a chemical treatment which would reverse the action of the cement. Sodium silicate was found to have practically no effect whatsoever. In other words, cement has the power of cancelling the viscosity—reducing properties of silicate. Quebrecho successfully lowered the viscosity to its normal value, and two other chemicals tested—namely sodium tannate and sodium gallate—were, if anything, better, although in the absence of cement their action was considerably less. Other chemicals which would be expected to have a

precipitant effect on the calcium were also examined, but were found to have practically no action whatsoever.

Theoretical Aspects.

In considering the mechanism of mud viscosity reduction from the theoretical point of view, one is concerned solely with that part of the fluid which is colloidal. The suspensoids which constitute the greater part of the clay are entirely inert as far as chemical treatment is concerned.

Numerous authors have used MacBain's concept of the micelle to account for the behaviour of mud fluid. The micelle was introduced to explain

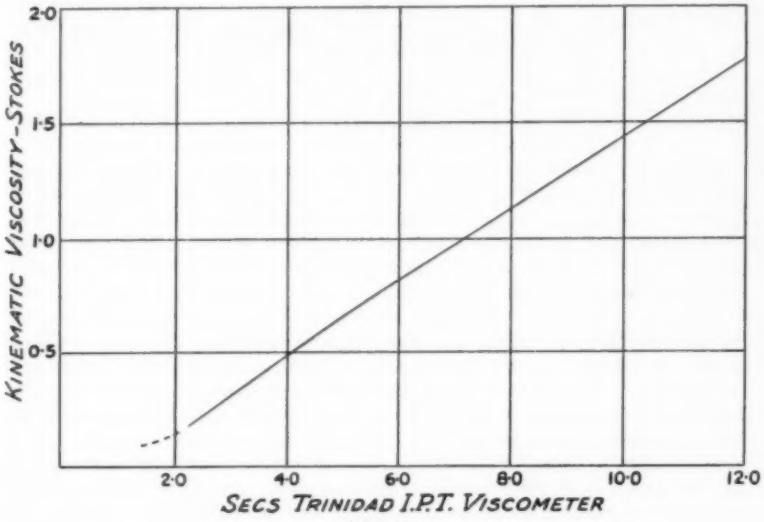


Fig. 6.

the abnormally high conductivities of soap solutions, and was conceived to be aglomeration of high-molecular-weight negative ions. It is, however, difficult to see how this can account for the phenomenon of thixotropy encountered in drilling muds.

A fibrillar theory is necessary to explain the observed results, and this requires the assumption of polarity of the individual clay particles. The fact that linear structures do exist in muds can be readily established visually. A very dilute suspension of mud shows striations corresponding to the currents in the liquid. Again a thick mud on stirring shows a modification in shade of colour in the path of disturbance. Both phenomena indicate the orientation of linear structures.

The gelling of mud can then be explained by the mutual attraction of the fibrils. The adsorption of the bivalent calcium ion would depend on the polarity of the individual clay particles, and would further increase gelling.

The effect of silicate and other sodium salts can be explained partly as

being due to the precipitation of bivalent ions and the resultant weakening of the forces between the clay particles.

Organic colloids which have so far proved to be the most effective viscosity reducers are evidently, in conjunction with the inorganic chemicals, able to completely surround the particles and to prevent their coalescence.

The whole phenomenon of thixotropy and the effect of chemicals is very complex and much work still remains to be carried out in order to explain the mechanism of the various reactions.

Acknowledgment is due to the Trinidad Petroleum Development Co. Ltd. for permission to use information included in the paper.

References.

[1] C. A. Andrews, *J.I.P.T.*, **21**, 963.
[2] P. Meyer, *ibid.*, **20**, 610.

DISCUSSION.

Mr. G. H. SCOTT congratulated the author on his paper. The author had stressed gel strength, which, in his opinion, was of fundamental importance. In practice the difference between the viscosity of the mud fluid as it entered the drillpipe and that of the outgoing mud was indicative of the rate of gel formation. Too large a differential not only increased the friction head, but also doubtless aided in the wall-building powers of the mud. It was obvious that those two viscosities could be kept more or less in balance by maintaining the area of the drill-pipe equal or approximately equal to that of the annulus. The speaker was convinced in his own mind that the advantages of drilling large holes were often completely neutralized by the formation of excessive thicknesses of the mud sheath and uneconomical use of available pump pressures.

The author appeared to favour the use of forest-clay mud of a weight of 80 lbs. per cu. ft., for mud-loading purposes, combined with chemical treatment if muds of a weight of over 110 lb. per cu. ft. were required. A forest-clay mud of 80 lb. per cu. ft. in the Fyzabad area was extremely viscous, and a mud of 85 lb. per cu. ft. as used by the author in his laboratory tests was almost unpumpable. That indicated that the forest clay in the Apex Field was definitely more colloidal, and that was further proved by the fact that a rise in viscosity with quebracho addition occurred at a much earlier stage than was shown in Figs. 3 and 4. Until recently the Apex used a forest-clay mud of 78 lb. per cu. ft. both for loading and when drilling with unloaded muds. That had been reduced to 72·5 lb. per cu. ft. With such mud, loaded muds of 115 lb. per cu. ft., with initial viscosities of 25 seconds I.P.T. viscometer, could be obtained without recourse to chemical treatment. Although the reduction in weight of the base mud required additional barytes, the low initial viscosities and the slow rate of gel formation rendered it of longer use in service, less liable to gas cutting and productive of higher drilling speeds. The speaker went further, and stated that an aquagel barytes mud of minimum gel strength would soon repay the extra initial cost of the barytes by permitting of smaller clearances for casing and by their increased life prior to extensive reconditioning,

especially if vibrating screens of small mesh were utilized to remove the maximum of clay cuttings.

In comparison with the United States practice, Trinidad muds were definitely too viscous, and the speaker's company had found that great benefits accrued from a reduction of the weight of base muds before loading.

The speaker was of the opinion that chemical treatment should be postponed as long as possible. With chemical treatment a condition was soon reached when even excessive additions of chemicals gave only minor reductions in viscosity. He had found that, in many cases, water dilution would effect great decreases in viscosity with only minor decreases in the mud weight, and was often advisable even when recourse was also had to chemical addition.

He would at that stage mention that they had found it advisable to carry out mud-loading and viscosity tests on all samples of barytes received. Barytes of identical specific gravities would often have widely varying mud-loading properties, while one sample, only slightly under their specification for specific gravity, yielded a mud of 100 lb. per cu. ft. which was quite unpumpable. It was interesting to note that the susceptibility of the latter mud to quebracho was only $\frac{1}{16}$ that of a normal mud of that weight.

It was noted that the author in his laboratory tests used a quebracho-caustic soda solution containing equal parts of those two substances. The speaker desired to ask him whether those proportions were used in practice. His field had a series of standard solutions with constant NaOH and varying quebracho for testing muds, and had found that a ratio of quebracho : soda of 16 : 10 by weight was generally most suitable. A 2 per cent. dosage of quebracho found by the author to be approximately the optimum, was also in excess of their requirements, and rarely was an initial dose of more than 1 per cent. of an equivalent solution necessary.

With regard to the author's remarks on the theoretical aspects, the speaker considered that the resemblance between clay suspensions and true colloidal dispersions could be over-stressed. Whilst resemblances doubtless existed, they were masked to a greater or less extent by the high proportion of inert suspensoids. Whilst doubtless a certain proportion of the colloidal material in a clay existed as emulsoid colloids in the dispersive phase, there must be some effect created by the surface characteristics of the particles and their mutual interactions.

Multivalent metal ions had a definite and major flocculating effect caused by agglomeration, be it of the fibrils or the negatively charged particles. In naturally occurring clays the most common of these were the bivalent Ca and Mg ions. Such agglomerations were deflocculated by sodium salts which were easily hydrolysed in aqueous solution. Such salts yielded alkali ions, which in themselves had a flocculating effect, and that must be inhibited by the addition of a protective colloid.

He was of the opinion that the action of sodium silicate and that of sodium tannate were identical; in one case the silica being the protective colloid and in the other the tannic acid. Silica, however, formed a strong gel at very low concentrations, and for that reason there would be great increase in the gel strength with increase in dosage.

The addition of protective colloids must have an optimum value for each clay suspension, dependent on the amount of colloids and alkali ions

originally present. Thus, continued chemical dosage had relatively little effect, as the reduction in viscosity caused by deflocculation was counterbalanced by the increased quantity of colloids in the suspension.

It should be specifically noted that commercial sodium silicate varied widely in its Na_2O content, and was also liable to considerable changes with age. It was therefore very inadvisable to use this substance in the field without preliminary laboratory tests.

On the relative quantity of metallic and alkali ions originally present depended the chemical treatment required. Sodium tannate had the advantage that the ionized tannic acid had a soft gel structure. It was therefore very suitable for oil-field use, as it could be used in excess with no marked increase in viscosity or gel strength. It was probable, however, that in the near future the molecular concentrations of the flocculating ions would be determined, and on their quantity the correct chemical treatment would be based.

Mr. H. C. H. Darley congratulated the author on an excellent paper.

He raised a question on the comparison of the Trinidad standard viscometer and the kinematic viscosity, and pointed out that the author had made no mention at all of mud weight or of shear strength on the curves.

Muds of totally different kinematic viscosity could be obtained which gave the same reading on the I.P.T. viscometer owing to difference in gravity or shear strength, *i.e.* their gel-forming quality. The speaker desired the author to give some standards for comparison of the two.

Another point was the question of 85-lb. mud. It did seem to him a bad and uneconomic policy to start off with a base mud at that weight. It was obvious that the ideal mud was definitely one in which there was suspensoid materials of maximum gravity, such as barytes, suspended by a minimum quantity of colloidal matter. This gives a very low initial viscosity, which has three definite advantages.

In the first place, it could pick up much more material from the well before it became unpumpable. In the second place, the rate of picking up suspensoid material was very much slower, that was to say, a high-viscosity mud would pick up material during drilling at a very much quicker rate than a low-viscosity mud. In the third place, there were the tremendous drilling advantages resulting from a low-viscosity mud. It seemed to him that the most economic policy was to start with a mud of minimum viscosity, and to keep it at that viscosity by treating whenever it showed a tendency to rise.

Mr. A. H. Richard congratulated the author on his paper, but said that there appeared to be one or two contradictions which he would like to have explained.

Firstly, the author told them that it was not found practicable to use shale mud drawn from drilling wells, and later on that it was only logical that measurements should be carried out in such a manner as to reflect field conditions as closely as possible.

It was stated that Andrews distinguished three types of linear flow, but it seemed that the condition of turbulent flow surely did exist in many places in the mud passages. The author referred to the initiation of tur-

bulent flow on the Trinidad I.P.T. viscometer, which he discounted as giving no true picture of viscosity. It seemed to the speaker that it was of importance to consider turbulent flow, which combined with other factors to make up the total resistance to pumping.

Subject to the author's reply to Mr. Darley's query about the character of the fluid used to obtain Fig. 6 in his comparison between kinematic viscosity and Trinidad I.P.T. seconds, it appeared to the speaker a contradiction of Mr. Bushe's statement that the latter apparently did not give a close enough reading. In the speaker's opinion the comparison was good. The author gave practically a linear relationship between the two, indicating that for the conditions under which the comparison was made that the I.P.T. viscometer gave good readings over a considerable range.

Again, the author said that the size of the orifice was varied in order that the tendency to gel during the time of flow was reduced to a minimum, and, in most cases, under optimum conditions of chemical treatment the fluid behaved as a true liquid, and this factor was of no importance whatever. The true meaning of that was very obscure to the speaker. If it indicated that the author was able to build up a mud to behave as a true liquid for given conditions, he had achieved something of very great importance in regard to pumpability.

Mr. Richard requested the author to give more data concerning the calibrated hollow glass rod.*

Mr. L. K. WHITE said that the author in his paper had referred to the chemical treatment of mud only in so far as loaded mud was concerned, with barytes as the loading material. It would be interesting to know if he had made any experiments with muds that were loaded with material other than barytes, and whether quebracho or silicate treatment of such muds was in any way comparable.

CHAIRMAN: Have you any loading materials in mind?

Mr. WHITE: None particularly, except the local clays used for loading mud.

Continuing, Mr. White said there was also the question of treatment of mud that was not loaded at all. In other words, the treatment of natural shale mud. On his field they had had some interesting experiences in treating shale mud. Some speakers that night had mentioned 80-85 shale mud as being too heavy. He was not quite sure why the author chose that weight for loading, but it was interesting in many cases to see how much the weight of pumpable shale mud could be brought up by quebracho treatment. Of course, the weight obtainable would be dependent on the nature of the clays or shales in which drilling was proceeding.

It had been found in some cases that the addition of barytes had been unnecessary—that the weight had been increased to such an extent that it was adequate for their purpose.

Mr. White thought there was a good deal to be said for the treatment of mud before loading. The Chairman had recommended postponing treatment until it was necessary. On the other hand, he thought something might be said for treating mud before loading, as it brought up the natural

* Glass rod: Diameter 0·90 cm. Length 27·5 cm. Weight 16·825 grm.

weight of the mud and brought down the viscosity practically to that of water, *i.e.* 17–18 seconds. The Trinidad instrument gave something like 15 seconds for water.

When proposals were made for introducing a better instrument for use on rigs, he would recommend that it be made even more simple and more robust than the Trinidad I.P.T. viscometer.

THE AUTHOR thanked Mr. Scott for his very interesting contribution to the discussion. He referred to the basic forest clay muds of 80–85 lb. per cu. ft. used in the experimental work, and mentioned that such weight muds would be of very high viscosity in the Apex field. This was equally true at Palo Seco. The author did not imply that such muds should be used initially for mud-loading purposes. During the course of drilling, shale cuttings are continuously being incorporated in the mud, and clay concentrations corresponding to 80–85 lb. per cu. ft. shale mud are soon obtained. Only then did chemical treatment become necessary, and it was that latter condition with which they were primarily concerned in Trinidad. In illustration, a well drilling recently in Palo Seco with 95 lb. barytes laden mud showed an increase in clay concentration from 75 lb. to 88 lb. per cu. ft. during the course of drilling. The above considerations also answered queries raised by other speakers.

With regard to the addition of water and the chemical treatment of mud, he was quite in agreement with Mr. Scott's remarks. It had frequently been found on the field that the addition of chemical after a certain point had very little effect on the mud; in fact, it might have an injurious action, whereas water if added would reduce the viscosity satisfactorily.

Regarding fluctuations in quality of barytes and its effect on the type of mud formed, the author had himself met with a sample of barytes, greyish in colour, which on analysis was shown to contain a small amount of lead sulphide. Weighed muds prepared with this material were normal in viscosity, but it was found that the addition of sodium silicate, which was in general use at the time, had no effect whatever in thinning the mud.

The proportion of quebracho to caustic soda used was based on laboratory experiments which indicated such a mixture to be the most efficacious. Mr. Darley questioned the direct comparison of the Trinidad I.P.T. viscometer readings and kinematic viscosity without considered mud weight and gel strength. Kinematic viscosity was independent of density. That quantity when multiplied by the density of fluid gave the absolute viscosity. Gel strength was certainly a factor influencing those measurements, but it was offset to a large degree when the rates of shear in the viscometer orifice were high.

In reply to the inconsistency which Mr. Richard found in the author's remarks on the impracticability of drawing mud from drilling wells and the desirability of reflecting field conditions closely, it should be pointed out that the conditions to be reproduced required an 80–85 lb. per cu. ft. clay mud, a fluid seldom if ever encountered in wells before the addition of barytes. In connection with turbulent flow, the author agreed as to its importance, but, on the other hand, it was clearly illogical to use an instrument which under certain conditions gave a true viscosity measurement and under other conditions gave a reading based on turbulent flow. Mr.

Richard was dubious about the author's reference to mud fluid as a true liquid. Reference to Figs. 2 and 4 showed that under optimum conditions of chemical treatment of the muds used, initial gel strengths were negligible. Once that disturbing factor had been eliminated it was reasonable to assume that the fluid behaved in the viscometer as a true liquid. When gelling appeared with thick mud, an attempt was made to minimize this variable by using larger orifices to increase the rate of shear.

In answer to Mr. White, experiments had been carried out with various local clays as a basis for drilling fluids. With suitable chemical treatment low-viscosity muds over 100 lb. per cu. ft. had been obtained. Unfortunately such fluids owe their viscosity to the relatively high percentage of coarse material, which is considered to be a most undesirable feature.

On the Chairman's proposal, a very hearty vote of thanks was accorded the author for his paper, and to the President and Members of the Apex Club for the use of their rooms.

THE POLYMERIZATION OF UNSATURATED HYDROCARBONS.*

By H. I. Waterman and J. J. Leendertse.

Synopsis.

An account is given of research which has been carried out in the Laboratory of Chemical Technology of the Delft Technical University, on the nature of the products formed by the polymerization of olefines and cyclic unsaturated hydrocarbons under various conditions. The polymerization products have been fractionated and hydrogenated and the fractions examined by the specific refraction–molecular weight method. These experiments furnish data on the amount of cyclization which accompanies "true" polymerization. Even polymerization with $AlCl_3$ as a catalyst at −78° C. was found in certain instances to bring about ring formation.

The specific parachor, a function of surface tension and density, has also been used for the characterization of fractions of different molecular weights.

The specific parachor–molecular weight method likewise enables data to be obtained on the degree of cyclization, but the specific parachor is also dependent on the ramification in the molecule, contrarily to the specific refraction which is practically independent thereof. A "number of rings" calculated from the parachor will differ from the true number of rings found by the specific refraction–molecular weight method. This difference gives an indication regarding the amount of branching in the saturated hydrocarbon molecules.

Introduction.

The production of hydrocarbon mixtures of increased molecular weight by polymerization † of unsaturated hydrocarbons is a process which has recently commanded general interest, particularly in view of its possible technical applications, such as the manufacture of gasoline, lubricating oil, resins, rubber, drying oils, etc.

In the following, a review is given of the results obtained in the Delft laboratory of Chemical Engineering by the polymerization of unsaturated hydrocarbons. The effects of structure of the base material and of reaction conditions on the composition of the reaction products have been studied, commencing from the conception that it is the "composition" of the products which determines their properties, including those properties which are important from a technical point of view. It may thus be assumed that an extensive, systematic investigation of the polymerization reactions in the long run will afford a clear and general idea of the suitability of certain polymerization processes (and, of course, other processes)

* Paper read at Second World Petroleum Congress, Paris, June 1937.

† Here, polymerization indicates increase in molecular weight together with the isomerization and dissociation processes connected therewith. "True polymerization" indicates the multiplication of the molecule of the base material, without the opening or forming of rings.

for making products having the desired (exactly specified) properties.[1] Such a research should take into consideration the effect of base material and polymerization conditions in the properties of the hydrocarbon mixtures formed, and also establish a direct quantitative relation between the composition and the properties of these mixtures.

In a research on this broad basis great difficulties are, however, experienced as the "determination of the composition" of the hydrocarbon mixtures considered constitutes in itself a complicated problem.

Determination of the composition of the complicated hydrocarbon mixtures, with which one has almost invariably to deal in petroleum chemistry, *by splitting the mixture into all its components* and subsequently identifying each component, may be considered to be practically impossible, especially in respect of the higher molecular hydrocarbon mixtures. Consequently it is obvious to try to find a solution by determining the *average composition of the mixtures as such*. In this connection the question then arises what is to be understood by "composition." The ultimate object being to establish a direct general relation between the properties of the hydrocarbon mixtures and their structure, the factors coming into consideration for determination are, in the first place, those factors in the structure of the hydrocarbons governing the properties in question.

In general, the properties of hydrocarbon mixtures to be considered besides the average molecular weight are:

(*a*) The average cyclic character.

(*b*) The average number of branches (or the number and nature of the side chains of the ring systems).

(*c*) The degree and nature of the unsaturation.

(*d*) An influence may also be expected from differences in the type of rings, and in the nature of the branches and from the presence of traces of "impurities," etc.

One of the authors, in co-operation with J. C. Vlugter and H. A. van Westen,[2] has worked out a simple method of determining the average cyclic character of hydrocarbon mixtures (*a*), such as gas oil and lubricating oil. This method, which also enables the aromatic content of olefine-free hydrocarbon mixtures to be estimated, may be utilized for studying the cyclic character of the polymerization products.[15] From the results given in the following, it will be seen that, if the properties of the hydrocarbon mixtures were to depend *solely* on the average cyclic character, it would be possible, by varying the initial material and conditions of polymerization, to comply with any demand for products having certain specified properties.

As already stated above, a knowledge of the cyclic character, or, in the case of hydrogenated products, the elementary composition of the product —depending on the number of rings—will not be sufficient for judging all the properties of the hydrocarbon mixtures. In the second part of this paper results are given of an investigation into the suitability of the parachor as a measure of the influence of branching on the properties of hydrocarbon mixtures. In this section, use was made of the series of polymers described in the first part of the article.

PART I.

THE CYCLIC CHARACTER OF SOME POLYMERIZATION PRODUCTS.

A number of aliphatic olefines (ethene, butenes, pentenes, octenes, decenes, hexadecene) and some cyclic unsaturated hydrocarbons (pinene, *cyclo*hexene and tetraline) have been utilized for the investigation. In most cases, aluminium chloride was used as the polymerization catalyst, only in a few cases were other catalysts, such as boron fluoride and aluminium oxide, applied. The work which has so far been completed deals mainly with polymerization at relatively low temperatures (−78° C. to about +70° C.), high temperatures being employed to a limited extent. The products obtained were liquids, except those obtained from pinene, which were partly solid (resins).

Details of most experiments can be found in the literature.[4-14] The following gives only some general remarks.

Experimental.

In all cases, practically pure hydrocarbons were subjected to polymerization.

When $AlCl_3$ was used as a catalyst, it was contacted with the hydrocarbon in the liquid phase by intensive stirring, and the temperature of the reaction mixture was controlled. The time of reaction was not the same for all experiments, but usually it was 3–5 hours. Separation into an upper layer poor in catalyst (" A oil ") and a lower layer rich in $AlCl_3$ (" B oil ") was observed except in the experiments carried out at −78° C. When polymerizing the cyclic unsaturated compounds, a relatively large quantity of " B oil " was invariably formed. In most cases " A oil " and " B oil " were examined separately after having been freed from catalyst by water washing. Both oils, after low-temperature fractionation, were tested by the specific refraction–molecular weight method.[2, 15] This method is based on the use of the specific refraction $\left(\frac{n^2-1}{n^2+2}\frac{1}{d}\right)$ of saturated hydrocarbon mixtures as a measure of elementary composition, and therefore of the cyclic character of the products. Since, however, most of the products of polymerization were slightly unsaturated, a careful non-destructive hydrogenation was necessary in order to complete the saturation. Cathode-light vacuum distillation with internal condensation [3] was employed for the above-mentioned separation of the reaction products.

In the experiments made with BF_3 as a catalyst, the latter was introduced as a gas into the liquid reaction mixture. With aluminium oxide as a catalyst, the hydrocarbon to be polymerized was passed over the catalyst in the gaseous phase.

No evolution of gas occurred during polymerization. Working with a series of polymers obtained from the same reaction product has the advantage of enabling the effect of molecular weight on composition to be observed, whereas variations due to the effect of incidental impurities are eliminated.

(a) *Experiments with $AlCl_3$ at about −78° C.*

In some cases, intensive polymerization was observed at low temperatures. *iso*Butene, for instance, reacted violently at −78° C.,[6] and asymmetric methylethylethene and trimethylethene showed a considerable degree of polymerization.[7]

With the aliphatic unsaturated hydrocarbons, a distinct difference in rate of polymerization was observed between the olefines of the type $-\underset{H}{C}=\underset{H}{C}-$ and those of the type $\equiv C-C=C-$ [11]. The polymerization activity of the latter is much greater than that of the former. (An analogous difference was observed when investigating the HCl addition to the olefines at about −78° C. without catalyst.[16]) At −78° C., the rate of polymerization of the olefines of the type $\equiv C-C=\underset{H}{C}-$ decreases rapidly with increasing molecular weight.[11] Polymerization at this low temperature may also give rise to ring formation: for instance, when polymerizing asymmetric methylethylethene, a product (mol. wt. 409) was obtained (after hydrogenation) which contained on an average one ring per molecule.[7] Ring formation was also observed [6] during polymerization experiments with *iso*butene at −35° to −40° C. Mention should also be made of the effect of a large quantity of hydrochloric acid on the action of $AlCl_3$, for, where $AlCl_3$ alone did not give rise to material polymerization, considerable quantities of higher-molecular products were formed [16, 5, 7, 10] on the addition of HCl gas.

(b) *Experiments with $AlCl_3$ at about Room Temperature.*

On the whole it may be stated that in the cases investigated (butenes, pentenes, a few octenes, decenes, hexadecene), a considerable yield of polymerization products was obtained with the exception of ethene, which reacts very slowly under these conditions and at atmospheric pressure. Among the unsaturated cyclic compounds investigated, pinene showed a very strong reaction,[12] but with *cyclo*hexene [10] and tetraline [14] the action was weak. In the polymerization of the aliphatic olefines liquid products were formed, whereas in the case of pinene the reaction products consisted partly of resins.[12] The products obtained from hexadecene are distinguished from the other polymerization products formed under analogous conditions by a relatively high molecular weight.

With aliphatic olefines, cyclization was invariably observed, except in the case of hexadecene. The relation of cyclization to the types of base materials and catalysts and to the average molecular weight of the fractions considered, can be readily seen from Fig 1 and 2. Fig. 1 shows the (idealized) change in specific refraction after hydrogenation of the polymer fractions in relation to their molecular weights. In this diagram, curve 1 represents the change in specific refraction of the series of paraffins, curve 2 that of the naphthenes containing one ring per molecule, etc., and curve 7 represents the change in specific refraction of " 100 per cent. ring " naphthenes of the condensed type. From the position of the curves for the series of polymer fractions, the number of rings per molecule and the

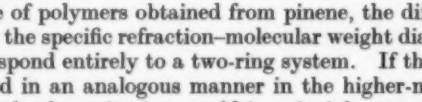
percentage by weight of the molecule part occurring on an average in the form of rings can readily be deduced for any molecular weight, assuming that the rings have been condensed (as *e.g.* in anthracene). Fig 2 shows, for the various series of polymers, the gain in rings (expressed in rings per molecule) for any molecular weight.

In the series of polymerizations of alpihatic base materials, " true " polymerization products, after hydrogenation, will invariably give a specific refraction situated on the paraffin curve. In the case of the cyclic hydrocarbons, " true " polymerization will cause the number of rings in the product to change proportionally to the molecular weight. On this basis Fig 2 has been constructed. When considering the results obtained, due consideration should be given to the small deviations which the specific refraction may show when compared with the elementary composition, and which amounts to about 0·1–0·2 ring per molecule. Consequently, care should be taken not to draw too far-reaching conclusions on the basis of the diagrams.

In the case of polymers obtained from pinene, the difficulty was experienced that in the specific refraction–molecular weight diagram, pinene itself did not correspond entirely to a two-ring system. If this deviation should be maintained in an analogous manner in the higher-molecular products, the progress of polymerization would in principle correspond to a " true " polymerization of the pinene, *i.e.* without rings opening or forming. If specific refraction were to give a correct picture, a considerable elimination of rings would have occurred. Further investigations have shown that it may be assumed that pinene does not undergo direct polymerization, but is converted first into a one-ring system, which then polymerizes whilst forming rings. In this connection the " true " polymerization of a pinene which would behave entirely as a two-ring system has been taken as basis for the curve in Fig 2.

(c) *Experiments with $AlCl_3$ at 50–70° C.*

In view of the slow rates of polymerization at low temperatures, tetraline[14] and *cyclo*hexene [10] were polymerized at higher temperatures, 50–70° C. On analysis, the *cyclo*hexene polymer showed a composition which may be practically entirely accounted for by the very probable " true " polymerization of *cyclo*hexene, in which the rings combine *e.g.* as follows :



When polymerizing tetraline,[14] the average composition of the product indicated a certain amount of ring opening and, by separation of a considerable quantity of a product containing three rings per molecule, it could be demonstrated that certain deviations from a " true " polymerization reaction had occurred.

(d) *Experiments with $AlCl_3$ at 125–150° C.*[4, 11].

When polymerizing ethene at 125–150° C. under increased pressure, considerable cyclization was observed and, in particular, the character of

the " B oil " was found to be highly cyclic. (This difference in character between " A " and " B oil " is not usually apparent, for in most of the cases investigated the cyclic character of the two oils was practically the same.)

(e) *Experiments with BF_3 as a Catalyst.*

For the polymerization of hexadecene at room temperature, BF_3 was used as catalyst in some instances.[11] Examination of the products obtained showed that polymerization had taken place to a smaller extent than in the experiment with $AlCl_3$ as catalyst. In this case too the products after hydrogenation were purely paraffinic.

(f) *Experiments with Aluminium Oxide as a Catalyst.*

In addition to the experiments described above with $AlCl_3$ as a catalyst, a polymerization was carried out on *iso*butene using aluminium oxide on silica gel as catalyst [17] at about 40° C.[8]

Contrary to the results of the experiments with $AlCl_3$, the degree of polymerization of the products was low, and no cyclization had occurred. The purely olefinic character of the hydrocarbon mixtures obtained rendered it possible to demonstrate the unsuitability of the McIlhiney bromine number determination for this group of compounds. The fact that this method gives much too low results has probably to be ascribed to HBr being separated from the dibromides formed by the addition of Br_2.[8]

Finally, some pentenes were heated to 400° C., with or without the above-mentioned aluminium oxide catalyst. At this temperature a fairly considerable polymerization was still observed, which, particularly in the case of pentene-2, was accompanied by a greater degree of cyclisation than was observed for the mixture of branched pentenes.

Conclusions.

From the foregoing, it is quite evident that $AlCl_3$ acts as a powerful polymerization catalyst, so that in some cases even at very low temperatures (about −78° C.) a considerable yield of high-molecular hydrocarbon mixtures could be obtained from low-molecular olefinic hydrocarbons. The action of $AlCl_3$ is not, however, limited to " true " polymerization, and in almost all cases examined secondary reactions were found to occur. For instance, when aliphatic olefines are polymerized with $AlCl_3$, cyclisation often occurs. In the series investigated, it was only hexadecene which yielded polymerization products which, after hydrogenation, gave purely paraffinic products. In this case, however, on account of the high molecular weight of the initial material, the chance of cyclisation is much smaller than, for instance, with ethene polymers. Cyclization may already occur at polymerization temperatures as low as −78° C. When polymerizing cyclic unsaturated hydrocarbons, ring opening was in some cases observed. The degree of cyclization of the products can easily be read from Figs. 1 and 2. From the position of the lines in these diagrams it may be concluded that by varying the base material and the conditions of polymerization, practically any desired composition (as far as it is expressed by the cyclic character) can be obtained, even more so when taking into con-

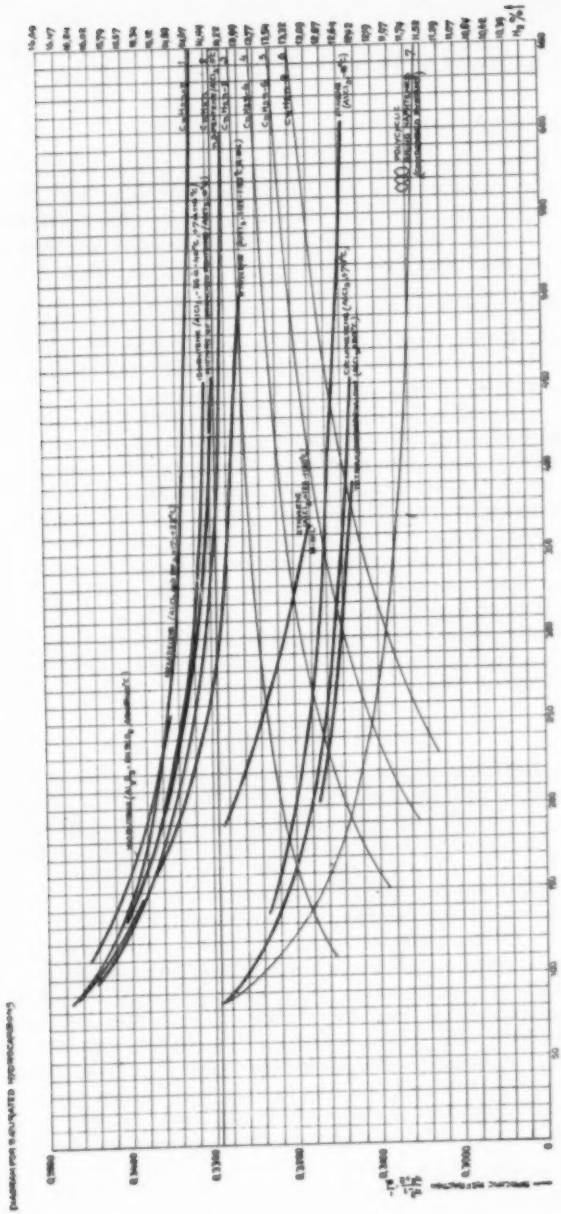


FIG. 1.

sideration that polymerization of mixtures of *e.g.* aliphatic and cyclic unsaturated hydrocarbons will considerably increase the number of possibilities. If, therefore, the properties of hydrocarbon mixtures should be governed solely by the cyclic character of the products, it would be possible

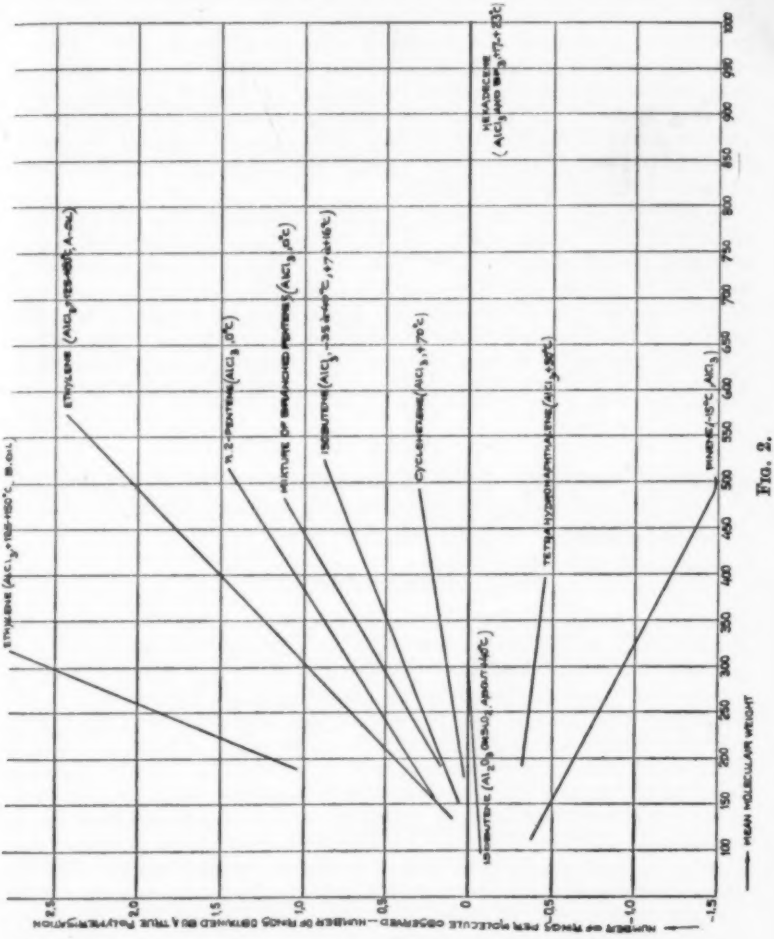


FIG. 2.

to comply with any demand for products having certain properties by polymerizing low-molecular unsaturated hydrocarbons.

Elementary analyses [15] have shown that the method applied for investigating cyclic character in the case of the (probably intensively branched) polymers does not give rise to deviations as a result of structure effects.

In such cases, where on an average more than one ring per molecule was found in some polymer fractions of aliphatic olefines without development of gas being observed during polymerization, it has to be assumed that cracking or dehydrogenation must have taken place in the reaction product during polymerization. With " true " polymerization of aliphatic olefines followed by a complete elimination of the unsaturatedness of the products by cyclisation, the number of rings per molecule cannot exceed one. By cracking or dehydrogenating the cyclic products, the degree of unsaturation required for further cyclization can then be attained. This involves, however, the presence of paraffinic, saturated hydrocarbons in another portion of the reaction product, which cannot be checked, however, owing to the lack of an easy and quick method of determining the degree of unsaturation of polymer mixtures.

In the foregoing, the production of high-molecular hydrocarbon mixtures of any desired " composition " by polymerization of low-molecular unsaturated hydrocarbons has been dealt with. It is also possible, however, to proceed inversely, and to produce lower molecular hydrocarbon mixtures from mixtures of hydrocarbons with high molecular weight. The composition of these lower molecular mixtures may likewise be greatly varied by suitable selection of base material and conditions of treatment.[18, 19] This applies also to the higher molecular polymerization products.[20]

PART II.

SURFACE TENSION AND THE PARACHOR IN CONNECTION WITH THE STRUCTURE OF SATURATED HYDROCARBON MIXTURES.*

Introduction.

As already stated in Part I, cyclic character alone will not always be decisive with regard to the properties of a hydrocarbon mixture. For instance, the octane number of gasoline and the cetene number of diesel oils are both greatly affected by the branching of the hydrocarbon chain. From published data, it may be assumed that branching effects in hydrocarbon mixtures will find expression in the parachor of these mixtures.[21] Heinze and Marder, for instance, tried to establish a direct relationship between the parachor of low-molecular hydrocarbon mixtures and their octane numbers [22] and between the parachor of diesel oils and their cetene numbers.[23] In view of the fact that in the investigations of Heinze and Marder, in addition to branching, the degree of unsaturation and the cyclic character of the products must also have affected the parachor of the gasolines and diesel oils considered, this work did not indicate clearly the effect of branching alone on the properties of the products. The work was, moreover, confined to relatively low-molecular hydrocarbon mixtures.

The authors having available, in addition to some series of hydrogenated fractions from natural oils, an extensive series of saturated hydrocarbon mixtures (described in Part I), it was decided to investigate to what extent

* Measurements of surface tension and calculations of the parachor values were mainly carried out by Mr. H. S. V. Bouwens.

the parachor would measure the degree of branching of the hydrocarbon mixtures. The influence of the unsaturation of the products was eliminated in this research by considering only completely hydrogenated mixtures, whilst, on the other hand, the cyclic character of the products was fully known as a result of the application of the specific refraction molecular-weight method.[2]

Surface Tension Measurements.

Measurements of the surface tension of the hydrocarbon mixtures were made according to the ring method (apparatus of Cenco-du Noüy[24]), and use was made of the correction table worked out by Harkins and Jordan.[25] Within melting-point limitations, all measurements were made at 20° C.

Some of the surface-tension measurements were checked by independent measurements using the stalagmometric method (when calculating the weight of the drops the correction table of Harkins and Brown[27] revised by Palitzsch[26] was applied). In practically all the cases considered, the difference in surface tension according to the two methods was below 0·5 per cent., the maximum difference found being 0·7 per cent. From these results, it could be concluded that *also for very viscid hydrocarbon mixtures the surface tension can be measured with an accuracy of about* 0·7 *per cent., corresponding to an accuracy of about* 0·2 *per cent. for the parachor considered below.*

The Surface Tension of the Saturated Hydrocarbon Mixtures.

Fig. 9 shows the idealized change in surface tension of various series of hydrocarbon mixtures with molecular weight. In each series the surface tension is seen to increase with increasing molecular weight, this being the case to the greatest extent with materials of relatively low molecular weight.

According to literature, surface tension is in general reduced by branching and increased by cyclization, and it is interesting that the order of the curves in Fig 9 in general confirms this rule.

As it may be expected that surface tension will not be quite regularly affected by the structure influences referred to (branching and cyclic character), the possibility of using the specific parachor was studied in more detail.

The Parachor of Hydrocarbon Mixtures.

Sugden[28] introduced the conception of molecular parachor $P = \frac{\sigma^{\frac{1}{4}}}{D - d} \cdot m$ in which σ = surface tension, D the specific gravity of the liquid at the temperature at which σ is measured, d the specific gravity of the vapour corresponding to the liquid under the conditions of measurement and m the molecular weight of the substance in question. In most cases, d is low as compared with D, so that the value of d may be disregarded. According to Sugden, the molecular parachor for pure substances is a constant which can be calculated additively from the elementary composition of the substance, and is dependent to only a small extent on the presence of branched chain hydrocarbons.

If Sugden's conceptions were entirely correct, it would be possible—on the basis of the atomic increments for a C and H atom and the ring

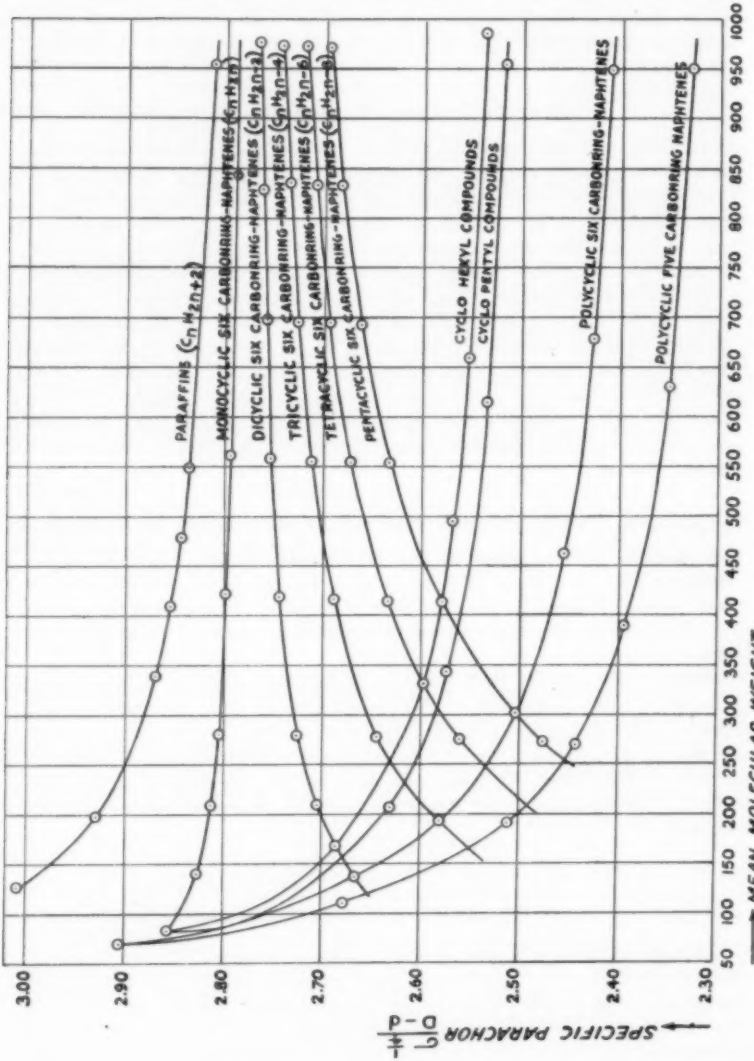

PARAFFINS (C_nH_{2n+2})
MONOCYCLIC SIX CARBONRING-NAPHTENES (C_nH_{2n})
DICYCLIC SIX CARBONRING-NAPHTENES (C_nH_{2n-2})
TRICYCLIC SIX CARBONRING-NAPHTENES (C_nH_{2n-4})
TETRACYCLIC SIX CARBONRING-NAPHTENES (C_nH_{2n-6})
PENTACYCLIC SIX CARBONRING-NAPHTENES (C_nH_{2n-8})
CYCLO HEXYL COMPOUNDS
CYCLO PENTYL COMPOUNDS
POLYCYCLIC SIX CARBONRING-NAPHTENES
POLYCYCLIC FIVE CARBONRING NAPHTENES
50 100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000
MEAN MOLECULAR WEIGHT
3.00 2.90 2.80 2.70 2.60 2.50 2.40 2.30
SPECIFIC PARACHOR $\frac{C}{D-d}$

FIG. 3.

increments given by Sugden—to construct a diagram for the saturated hydrocarbons in which the molecular parachor is plotted for various homologous series (paraffins, naphthenes containing one ring per molecule,

etc.) as a function of the molecular weight. For practical reasons it is recommended that the *specific* parachor $\left(\frac{\sigma^{\frac{1}{4}}}{D-d}\right)$ should be applied for this purpose. Fig. 3 shows such a diagram, the six-membered ring having been taken as the standard type for calculating the curves.

If it were possible to consider the specific parachor of hydrocarbon mixtures as a perfectly additive function of the specific parachors of the components (as is the case with the specific refraction), then *Fig.* 3 *could be used for judging the elementary composition and consequently the cyclic character of the fully saturated hydrocarbon mixtures.*

Elementary analyses have proved that the specific refraction of saturated hydrocarbon mixtures is a satisfactory measure of the elementary composition of these mixtures.[2, 15] Thus, by determining the average number of rings per molecule of the saturated mixtures considered, with the aid of the specific refraction and specific parachor diagrams, it may be ascertained whether the specific parachor constitutes a means for estimating the elementary composition. If Sugden's conceptions were true, the same number of rings should be found in the two diagrams. *In many cases, however, the desired agreement was not found for the hydrocarbon mixtures considered.*

For some of the series of saturated products in question, the deviations are clearly shown in Fig. 4, in which the difference in ring number derived from the specific parachor and the specific refraction has been plotted (in this and following diagrams the curves drawn as straight lines represent somewhat idealized conditions). The actual cyclic character of the series of polymers considered in Fig. 4 and in those following, is shown in Fig. 1. In many cases the number of rings indicated by the specific parachor was higher than that given by specific refraction, except in the cases of the hexadecene polymers and Rangoon paraffin wax, for which a negative, and thus impossible, ring content was found.

Since the source of the deviations need not be sought in the specific refraction–molecular weight diagram,[2, 15] the most obvious explanations appear to be:

a. Irregularities which are liable to occur owing to the fact that mixtures, and not simple substances, are considered.

b. Deviations due to incorrect values of the atom-increments given by Sugden.

c. Deviations due to the influence of special structures on the specific parachor, *e.g.* of the branching of the hydrocarbon chain.

Although the authors have not yet sufficient data for complete checking of the additivity of the specific parachor, it can nevertheless be stated that the results obtained are not materially affected by factor *a*, so that the causes mentioned under *b* and *c* are left as explanations. It is practically impossible to explain all deviations by assuming errors to occur only in Sugden's atomic parachors, *so that it is to be concluded that the specific parachor of a compound is not entirely independent of atomic linkage.* Conversely, this implies that the method of calculation applied by Sugden for determining the atomic parachors is not quite correct, since the effect of differences in structure has been disregarded. Mumford and Phillips[21]

have already directed attention to this fact, and have re-calculated the atomic parachor values. These investigators ascribe a definite effect to the occurrence of branching, and, with respect to the presence of a tertiary

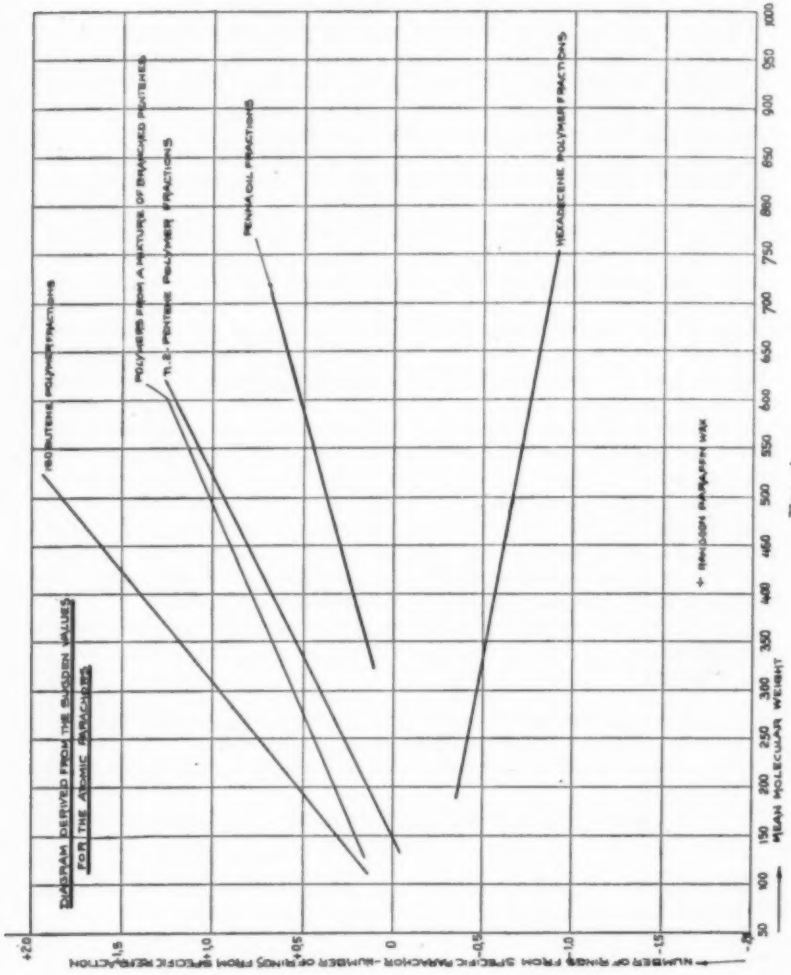

ISOBUTENE POLYMER FRACTIONS
POLYMERS FROM A MIXTURE OF BRANCHED PENTENES
N.-B.-PENTENE POLYMER FRACTIONS
PENNSYLVANIA OIL FRACTIONS
HEXADECENE POLYMER FRACTIONS
+ RANGOON PARAFFIN WAX
DIAGRAM DERIVED FROM THE SUDDEN VALUES FOR THE ATOMIC PARACHORS
+2·0
+1·5
+1·0
+0·5
0
-0·5
-1·0
-1·5
-2·0
NUMBER OF RINGS FROM SPECIFIC PARACHOR - NUMBER OF RINGS FROM SPECIFIC REFRACTION
50 100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000
MEAN MOLECULAR WEIGHT

FIG. 4.

C atom, introduced a parachor increment (for the molecular parachor) of — 3·0.

Although the number of reliable parachor values for pure defined hydrocarbons is too small to allow of checking the work of Mumford and Phillips in every respect, *in our opinion it is more correct, especially in view of the*

results described above, to base our considerations on the atomic parachor values of Mumford and Phillips. The results thus obtained are so favourable that their values will probably require but little correction.

With the aid of the last-mentioned atomic parachor values of Mumford

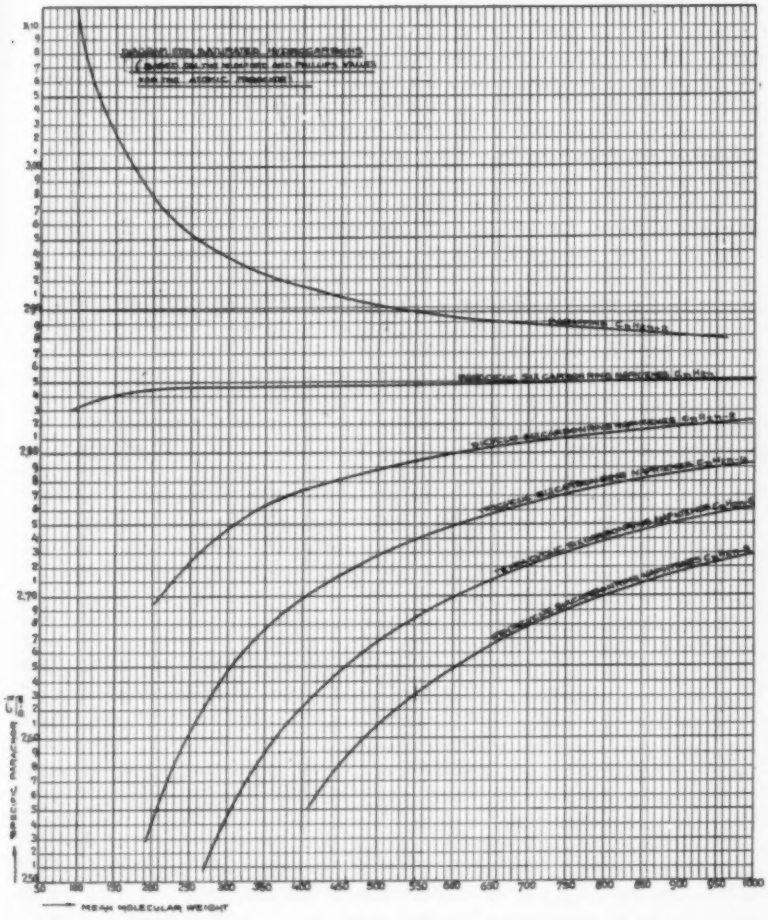


FIG. 5.

and Phillips, a new specific parachor–molecular weight diagram was constructed for saturated hydrocarbons (Fig. 5). The least possible branching was invariably assumed for calculating the curves for the various homologous series; *i.e.* (*a*) no tertiary C atom in the series of paraffins, (*b*) one tertiary C atom in the series of monocyclic six-ring naphthenes,

(*c*) three tertiary C atoms in the series of dicyclic six-ring naphthenes, etc. It was then possible to re-determine for the saturated products the difference between the number of rings derived on the one hand from the specific parachor (Fig. 5) and on the other hand from the specific refraction (Fig. 1). This difference is shown in Fig. 6, which also includes differences for various hydrogenated *natural* oils.

From a closer examination of the results given in Fig 6 it follows, firstly, that the differences in the numbers of rings derived from the specific refraction and the specific parachor have in general increased when compared with those of Fig. 4, and secondly, that the negative quantities of rings per molecule, as derived from Fig. 3 for the hexadecene polymers, have changed to small positive quantities of rings, and also that the considerable negative amount of rings for Rangoon paraffin wax has become much smaller. For products obtained by polymerization of tetraline and *cyclo*hexene, the numbers of rings derived from the specific refraction and from the specific parachor are practically equal. All products obtained by polymerization of the aliphatic olefines gave a much higher ring content according to the specific parachor than according to the specific refraction. For each of the series these deviations in amount of rings increase with the molecular weight of the fractions considered; the greatest deviation occurring in the curve of the *iso*butene polymers, followed successively by the ethylene polymers, the polymers obtained from a mixture of branched pentenes, the *n*-pentene-2 polymers and the hexadecene polymers. On the whole, the natural oils show considerable deviations, which are spread over a wide range about the curve for the Penna-oil fractions. According to the views of Mumford and Phillips,[21] it should be possible to explain the "*apparent extra cyclic character*" (found for the various products by comparing the composition according to the specific parachor and according to the specific refraction) by differences in branching of the products.

The disappearance of the improbable negative amount of rings in the hexadecene polymers according to Fig. 3 gives countenance to the greater correctness of the newly developed system. The Rangoon paraffin wax, however, still shows a certain deviation, but as the determination of the parachor was made at 60° C., and the specific parachor being somewhat susceptible to temperature changes, a slight correction to the value of the Rangoon paraffin wax is still necessary. As the specific parachor for several hydrocarbons has been proved to decrease with decrease in temperature, the deviation observed in Fig. 6 will become smaller at 20° C.

The supposition, put forward on the basis of specific refraction, that the polymerization of *cyclo*hexene is a "true" polymerization, agrees with the results derived from the specific parachor. The number of side-chains or branches to be expected in the polymerization of tetraline is also small,[29] this again being in agreement with the results derived from the specific parachor. It is, however, quite plausible that in the series of polymers obtained from aliphatic olefines, highly branched systems occur, and this is in some cases borne out by literature.[30] The order of the deviations in Fig. 6 for the series of polymers derived from various substances, mostly obtained under analogous conditions, is reconcilable with the assumption that the parachor is affected by branchings. Very intensively

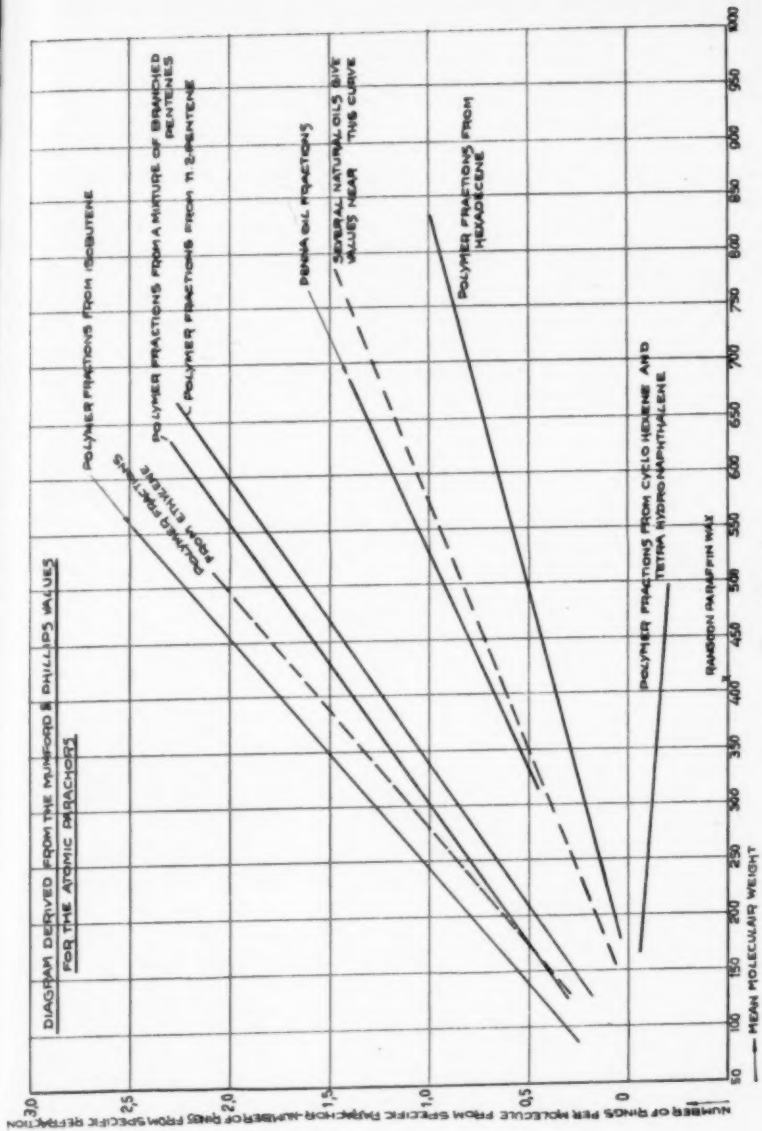


DIAGRAM DERIVED FROM THE MUNFORD & PHILLIPS VALUES FOR THE ATOMIC PARACHORS
POLYMER FRACTIONS FROM ISOBUTENE
POLYMER FRACTIONS FROM A MIXTURE OF BRANCHED PENTENES
POLYMER FRACTIONS FROM N. 2-PENTENE
PENNA OIL FRACTIONS
SEVERAL NATURAL OILS GIVE VALUES NEAR THIS CURVE
POLYMER FRACTIONS FROM HEXADECENE
POLYMER FRACTIONS FROM CYCLO HEXENE AND TETRA HYDRONAPHTHALENE
RANGOON PARAFFIN WAX
POLYMERIZED SPECIMENS FROM ETHYLENE
NUMBER OF RINGS PER MOLECULE FROM SPECIFIC PARACHOR-NUMBER OF RINGS FROM SPECIFIC REFRACTION
MEAN MOLECULAR WEIGHT
3,0
2,5
2,0
1,5
1,0
0,5
0
50
100
150
200
250
300
350
400
450
500
550
600
650
700
750
800
850
900
950
1000

FIG. 6.

branched systems are to be expected when polymerizing *iso*butene. In the case of ethylene, branching is somewhat less liable to occur, but here again the chances of intensive branching and cyclization are considerable, owing to the small base molecule. Next follow the series of polymers from a mixture of branched pentenes, from *n*-pentene-2 (in which a fairly intensive branching is also to be expected in view of the position of the double bond) and, finally, from the hexadecene. It is not improbable that the products obtained from hexadecene show some branchings, since branching of the polymerization products is to be expected when the polymerization occurs at non-terminal carbon atoms of the hexadecene.

In addition, the utility of the "apparent extra cyclic" character of saturated hydrocarbon mixtures for judging the degree of branching of the products is confirmed by the results obtained for some highly cyclic oils of relatively low molecular weight. The number of possible extra branches in these compounds is small, so that in these cases no considerable differences should be found between the numbers of rings according to the specific parachor on the one hand and according to the specific refraction on the other. As is evident from Table I, these oils show but slight deviations.

TABLE I.

Molecular Weight.	Specific Parachor.	Specific Refraction.	Number of Rings per Molecule.		Difference in Rings.	Composition of the Oil.	
			From Specific Parachor.	From Specific Refraction.		% Paraffin.	% Naphthene.
305	2·579	0·3169	3·7	3·5	0·2	30	70
254	2·615	0·3188	3·0	2·7	0·3	35	65
170	2·670	0·3200	2·0	2·0	0	22	78
191	2·714	0·3238	1·8	1·7	0·1	42	58
177	2·694	0·3218	1·9	1·9	0	32	68
202	2·726	0·3245	1·8	1·6	0·2	48	52
209	2·650	0·3204	2·3	2·2	0·1	33	67

Since, in view of the above, it is feasible that the specific parachor, when compared with the specific refraction, affords an idea of the degree of branching, it is also possible, from the work done by Mumford and Phillips, *to calculate the total number of extra branches occurring on an average in the saturated mixtures considered.*

The calculation of this "extra" * number of tertiary C atoms is greatly facilitated by the fact that a difference of 0·1 ring per molecule, according to the specific parachor and the specific refraction, corresponds fairly well to 1 "extra" tertiary C atom. Thus Fig. 6 can be used for determining the total number of "extra" tertiary carbon atoms.

An even better idea of the degree of branching of saturated hydrocarbon mixtures is afforded by the number of "extra" tertiary C atoms occurring on an average in the paraffinic part of the molecule with a molecular weight 100

* By "extra" branches are meant the branches which have not been taken into account in the calculation of Fig. 5. Therefore in the case of the ring systems, the presence of more than one side-chain may also be included,

and equalling the total number of "extra" tertiary C atoms $\times$ $\frac{100}{\%\text{ paraffin rest}} \times \frac{100}{\text{mol. weight}}$.

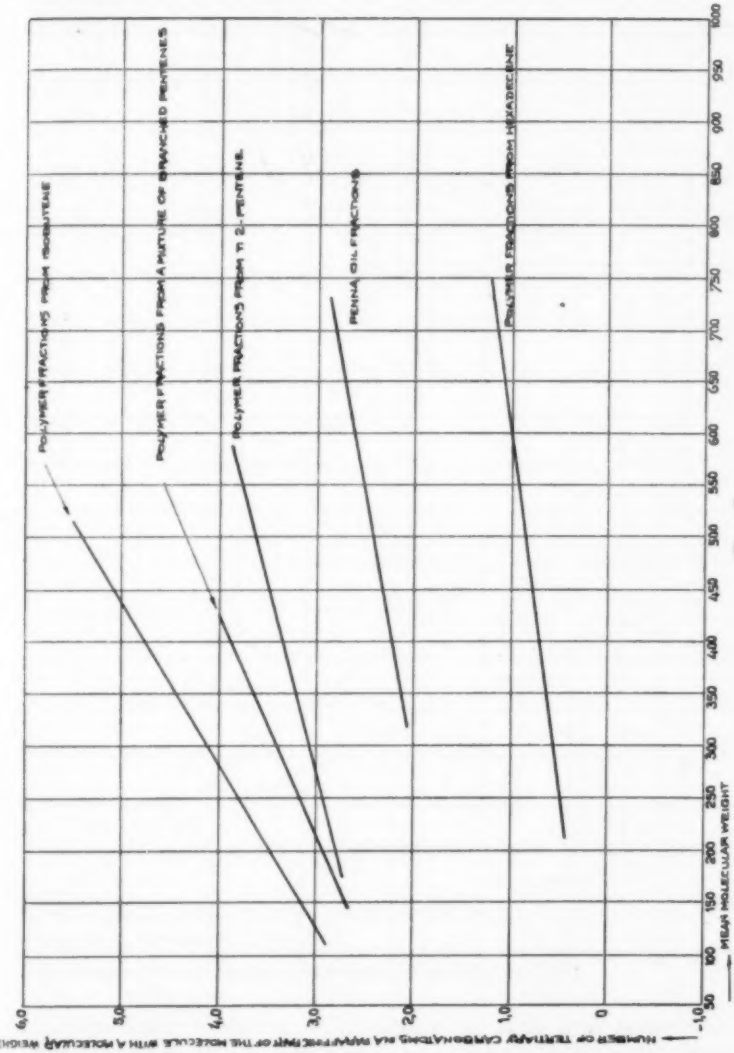


Fig. 7.

For some of the series of products investigated, this number is given in Fig. 7. Here it is seen that the figure indicating the degree of branching is exceptionally high for *e.g.* isobutene polymers, particularly for

the fractions of relatively high molecular weight. *It should, however, be stressed that too far-reaching conclusions should not be drawn from the calculations of the above figures for the number of "extra" tertiary C atoms. The*

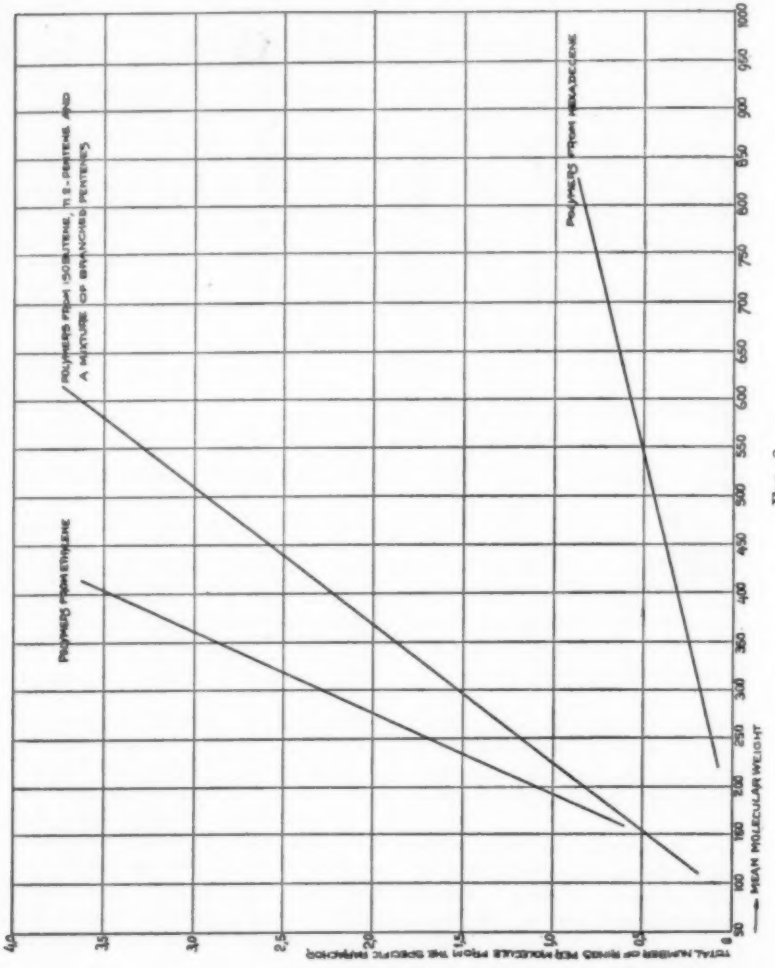

POLYMERS FROM ISOBUTENE, TRIMETHYL ETHYLENE AND A MIXTURE OF BRANCHED PENTENES
POLYMERS FROM ETHYLENE
POLYMERS FROM HEXADECENE
MEAN MOLECULAR WEIGHT
TOTAL NUMBER OF RINGS PER MOLECULE FROM THE SPECIFIC PARACHOR

FIG. 8.

experimental basis is as yet insufficient for the general application of the atomic increment of — 3·0 for a single branching, and the errors of observation in the specific parachor and slight deviations of the specific refraction with respect to the elementary composition of saturated hydrocarbons in certain cases may have a fairly considerable effect. For instance, the numbers of rings

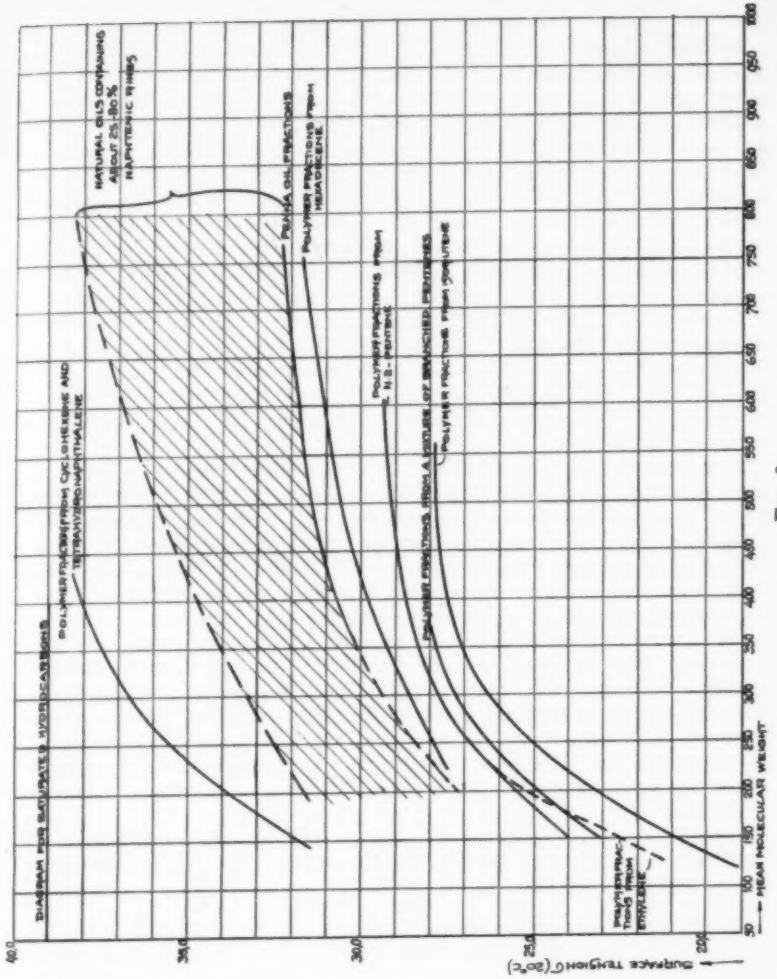


FIG. 9.

per molecule according to the specific parachor and the specific refraction may show a difference of about

0·1 — 0·2	ring	for a	molecular	weight	<200
0·2 — 0·3	,,	,,	,,	,,	200–400
0·3 — 0·4	,,	,,	,,	,,	400–600
0·4 — 0·6	,,	,,	,,	,,	600–1000

This applies in particular to the examination of separate hydrocarbon mixtures. The accuracy will be much more satisfactory for a series of fractions obtained from one and the same reaction product.

FIG. 8.

Conclusions.

By comparing the composition of saturated hydrocarbon mixtures, as derived from the specific refraction and the specific parachor diagram (the latter based on the atomic parachors of Mumford and Phillips), it is possible to form a qualitative idea of the degree of branching of the hydrocarbon mixtures considered. This method is particularly suitable for judging the branching of mainly aliphatic hydrocarbon mixtures. With respect to the range of highly cyclic oils, it is usually a little more difficult to reach conclusions, as in that case the specific parachor may be affected not only by the effects of branching, but also by differences in ring type. (In the case of unsaturated hydrocarbon mixtures, these should be converted into saturated mixtures beforehand by careful analytical hydrogenation.)

Owing to the number of parachor values of pure hydrocarbons described in literature being very small, it cannot yet be fully ascertained as to how far the number of branches found in the manner described above agrees *quantitatively* with the actual number of branchings of the hydrocarbon mixtures. An extension of the research with pure high-molecular hydrocarbons is necessary.

Nevertheless, the " apparent extra cyclic character " or the " number of extra tertiary carbon atoms," and the " number of extra tertiary carbon atoms in a paraffinic part of the molecule with a molecular weight 100 " constitute average figures directly related to the manner in which one of the physical properties of the mixtures is affected by certain molecular structures. Thus it may be expected that they can be used successfully for judging other definite properties of hydrocarbon mixtures.

As regards such properties as are affected by both cyclic character and branching, the " *apparent total cyclic character* " derived from the specific parachor will probably play a part. Fig. 8 gives a comparison of this " apparent total cyclic character " of some series of polymerization products, and here it will be seen that the *iso*butene and *n*-pentene-2 polymers and the polymers obtained from a mixture of branched pentenes show the same change in " apparent total cyclic character " with the molecular weight.

Finally, it can be remarked that with nearly all partly cyclic natural oils, including Penna oil, there might be present ring systems with fairly intensively branched side chains.

Laboratory for Chemical Technology
of the Technical University, Delft. *February* 1937.

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THE VISCOSITIES OF HYDROCARBONS.

By E. B. Evans, Ph.D., M.Sc. (Member).

PARTS I–III.*

Synopsis.

During the last half-century a large amount of experimental data on the viscosities of hydrocarbons has been accumulated during the course of numerous investigations into the relationship of chemical constitution and viscosity and the dependence of viscosity on temperature. More recently results have been published on some of the hydrocarbons of higher molecular weight and more complex structure, such as might be expected to occur in the higher-boiling fractions of petroleum, and especially in lubricating oils.

An attempt has been made here to review critically this mass of data and to present the most reliable and accurate of the results in tables showing viscosities in absolute and in kinematic units at certain standard temperatures, viz. 0° C., 20° C., 50° C., 80° C. and 100° C. The figures tabulated have been obtained by plotting the available experimental data and using the values obtained from these curves.

The results are then readily available for the examination of constitutional or temperature effects on about 150 hydrocarbons, including 38 which have been examined experimentally in the course of this work.

Parts I–III deal with the general method of the investigation, the measurement of viscosity and some considerations on small viscometers, and the viscosities of the normal paraffin hydrocarbons, respectively. Subsequent parts to be published later will consider the *iso*paraffins, monocyclic naphthenes, acyclic and cyclic naphthenes, monocyclic aromatics and polynuclear compounds; while in the last paper constitutional relationships will be examined. Viscosity–temperature relationships have already been discussed elsewhere.

PART I.

Introduction.

Most of the applications of petroleum products, whether as fuels or lubricants or for numerous other purposes, depend to a considerable extent on viscosity and on rate of change of this property with temperature. The viscosity characteristics of petroleum oils vary widely with their composition, and since this not only depends on the source of the crude from which the oil is derived, but can be controlled quite largely by the refining processes to which the oil is subjected, a knowledge of the viscosity characteristics of the hydrocarbons composing petroleum is of very considerable importance.

A great deal of work has been done during the last eighty years or so on the fundamental nature of the viscosity of liquids and its dependence on temperature and on the constitution of the liquid concerned. In the present work only hydrocarbons will be considered, as this class of compound is chiefly of interest in regard to petroleum and its products. Moreover, the problems involved are complicated, even with carbon and hydrogen

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only present, and with the inclusion of other elements in the molecule, constitutional effects become even more difficult to distinguish.

In discussing the viscosity of hydrocarbons in relation to petroleum products, one of the greatest difficulties has been that the amount of data available has been small, and that much of it has been recorded in a form not readily usable, has been of doubtful accuracy or has not covered a sufficient range of temperature.

The present series of papers deals with the collection and critical evaluation of the data on hydrocarbon viscosities which are available from the literature, together with the results of determinations on thirty-eight hydrocarbons which have been examined in order to extend the information on this subject. Following this introductory paper, the methods of viscosity measurement used in the experimental part of the work are described, together with some discussion of the errors associated with small viscometers of the Ostwald type. Succeeding papers describe the data on hydrocarbons, class by class, and finally hydrocarbon viscosity and chemical constitution are considered. Much of the data here recorded has been utilized in a study of viscosity–temperature relationships, which has been published elsewhere.[1]

Most of the data on hydrocarbon viscosities which have been recorded are expressed in poises or centipoises. The temperatures which have been used for the measurements are, however, varied, and are often not multiples of whole degrees. In order to render this mass of data usable for purposes of comparison, and for examination in attempts to deduce useful relationships, the recorded results have been plotted and values for the viscosities read off in centipoises from the smoothed curves, at definite temperatures. The temperatures selected for this work are 0° C., 20° C., 50° C., 80° C. and 100° C., although in some cases it has not been possible to include results at the extreme temperatures of the range 0–100° C., on account of the limited range covered by the data. Sometimes extrapolation has been employed to obtain figures at the stated temperatures, but this has been done only where the experimental accuracy of the results appeared to justify the procedure. Where the extrapolation has been considerable, the figures concerned are enclosed in brackets in the Tables of Data. It will be noted also that in some cases viscosities are tabulated, for comparative purposes, at temperatures below the melting point, or above the boiling point of the hydrocarbon concerned.

In compiling the above tables, only data have been used which are considered to be of sufficient accuracy. In some cases only one set of data is available and then the accuracy has been judged by the regularity of the plot obtained, by the physical data (if any) recorded for the compounds investigated, by the methods used for viscosity determination, and by any other indications of the general accuracy of the work concerned. Where data for a hydrocarbon have been recorded by more than one author, a comparison often enables the more reliable results to be selected.

For a number of compounds, results have been recorded at one temperature only and, particularly where this temperature is not one of those normally used, the data are of greatly reduced value. Similarly, where no physical data or indication of the source of the hydrocarbon used are given, it is difficult to assess the value of the work. The absence of density data

in many cases is particularly unfortunate, since in view of the increasing tendency to express viscosities in kinematic units (centistokes), the results may be required in this form. In the succeeding sections of this work the data are recorded where possible in kinematic units also, together with the appropriate density data. This conversion has been rendered much more difficult by the absence of physical data in many papers on hydrocarbon viscosity, and densities have had then to be obtained from other sources.

It cannot be too strongly urged that all investigators recording hydrocarbon viscosities, either in centipoises or centistokes, should include also, among other physical constants, densities at two or more temperatures. Results should also be determined at even temperatures over as great a temperature range as possible. Observance of these practices would greatly enhance the value of the data to other workers in the field, and permit also critical evaluation and comparison with data from other sources.

As regards the method of plotting data which has been employed in this work, in many cases the equation of Andrade [2]

$$\eta = Ae^{b/T}$$

has been used. Plotting was carried out on a large scale, and the use of the logarithm of the absolute viscosity against the reciprocal of the absolute temperature often gave lines of a sufficiently low degree of curvature to enable the necessary amount of extrapolation to be carried out. More complicated equations had to be used, however, for viscous hydrocarbons, in order that extrapolation might be possible.

For compounds (such as those examined by Mikeska, recently) where the results are given in centistokes, the chart of Ubbelohde [3] has proved very useful, as the main graduations of this viscosity chart are in centistokes and degrees centigrade.

PART II.

The Measurement of Viscosity.

A large number of viscosity measurements on hydrocarbons have been carried out in the course of this work. The instrument first used was a B.E.S.A. (now B.S.I.) Number 1 Viscometer of the Ostwald type, as described in Specification No. 188 of 1929, but modified by the introduction of a finer capillary for that originally in the instrument. The modification was in order to reduce kinetic energy effects and render the viscometer suitable for use with liquids of very low viscosity. The time of flow for water at normal temperatures was thereby increased from about 100 to about 190 seconds.

A number of measurements were made with this instrument, including many on hydrocarbons for which accurate viscosity data were available from the literature. On comparison of the results obtained, discrepancies of up to about 3 per cent. were found. These differences were much greater than could be accounted for by kinetic energy effects, and it was therefore suspected that the viscometer was subject to some source of error which had hitherto been overlooked.

Tables I and II give the results of calibration of this viscometer, and also

an unmodified B.E.S.A. No. 1 viscometer, using water and also various carefully purified hydrocarbons, the viscosities of which were taken from reliable sources in the literature. The results are expressed as values of k in the equation $\eta = k \,.\, t \,.\, d$, and as the percentage value of this "constant" on the value obtained by calibrating with water at 20°. The kinetic energy error is larger in the case of the unmodified viscometer, but in no case does it approach the magnitude of the errors found.

TABLE I.

Calibration Results with Modified B.E.S.A. Viscometer.

Calibrating Liquid.	Viscosity in cp.	Authority.	Value of k.	$\frac{k}{k \text{ for Water}} \times 100.$
Water at 20° C.	1·0087	I.C.T.	0·005929	100·0
Benzene at 20° C.	0·647	I.C.T.	0·005834	98·4
2 : 2 : 4-Trimethylpentane at 20° C.	0·503	Smyth and Stoops	0·005768	97·3
n-Heptane at 20° C.	0·409	Smyth and Stoops	0·005753	97·0
	0·4093	Thorpe and Rodger		
n-Heptane at 25° C.	0·3859	Shepard, Henne and Midgley	0·005710	96·3
	0·3855	Lewis		

TABLE II.

Calibration Results with B.E.S.A. Viscometer.

Calibrating Liquid.	Viscosity.	Authority.	Value of k.	$\frac{k}{k \text{ for Water}} \times 100.$
Water at 20° C.	1·0087	I.C.T.	0·01195	100·0
n-Heptane at 20° C.	0·409	Smyth and Stoops	0·01179	98·7
		Thorpe and Rodger		
*cyclo*Hexane at 15° C.	1·050	Timmermans and Martin	0·01161	97·2

These results were communicated to Dr. G. Barr of the National Physical Laboratory in May 1933. Dr. Barr informed us that he had already noticed errors of this kind in connection with the No. 1 Viscometer and was publishing a note on the subject at the forthcoming World Petroleum Congress.[4] Barr considers that the errors are due to the large surface–volume ratio of viscometers with small bulbs, so that the effect of surface tension on the hydrostatic head is relatively great.

Acting largely on suggestions from Dr. Barr, viscometers have been designed which avoid the errors of the B.E.S.A. No. 1 instrument and allow very accurate determinations of the viscosities of thin liquids to be made. The dimensions of the viscometers are given in Table III and in Fig. 1. The general specifications (details of glass, construction, etc.) are the same as for the B.E.S.A. series of viscometers. Viscometers similar to those described here, except for slight modifications in capillary diameter, have since been adopted by the Institution of Petroleum Technologists ("Standard Methods of Testing," 3rd Edition, 1935, p. 171) and by the B.S.I. (Specification No. 188 of 1937).

Two viscometers were employed to cover the whole of the desired range

TABLE III.

Dimensions of Viscometers Used.

Length *aB*	6 cm.
Length capillary *de*	12 cm.
Internal diameter of *de*	0·048 cm. for No. 1 Viscometer 0·062 cm. for No. 2 Viscometer
Internal diameter of *aB*	0·5 cm.
Capacity of Bulb *BC*	6·5 ml.
Internal diameter of *BC*	2·0 cm.
Capacity of Bulb *CD*	0·4 ml.
Internal diameter of *ef*	0·5 cm. min.
Internal diameter of *Gh*	0·5 cm.
Bulb *fG*, internal diameter	2·0 cm. min.
Bulb *fG*, capacity	7·0 ml. min.
Distance from middle of *BC* to *G*	8·0 cm.
Distance between vertical axes	1·7 to 1·8 cm.
Vertical distance of *M* above *G*	2·5 cm.

from about 0·4 to 16 centistokes. The first has a capillary diameter of 0·048 cm. and the second of 0·062 cm., the times of flow of water at 20° C. being 635 and 226 seconds respectively.

aB	6 cm.	
de	12 cm.	
I.D. of *de*	0·048 cm.	Viscometer (1)
	0·062 cm.	Viscometer (2)
I.D. of *aB*	0·5	
BC capacity	6·5	
BC, I.D.	2·0	
Cd capacity	0·4	
Tube *ef* min. I.D.	0·5 in.	
x	10·0 cm.	
Axial diff.	1·7/1·8 cm.	
MG	2·5 cm.	
I.D. of *Gh*	0·5	
fG min. capacity	7·0	
fG min. I.D.	2·0	

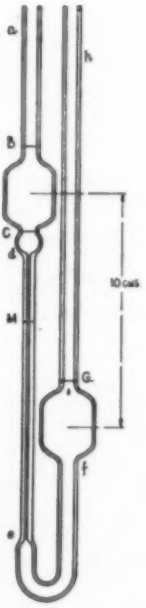

FIG. 1.

VISCOMETER FOR HYDROCARBON MEASUREMENTS.

The kinetic energy correction is not large on these instruments, being approximately 0·36 per cent. and 0·95 per cent., respectively, for water in the two viscometers. The percentage error due to kinetic energy is given by the expression:

$$\frac{m \cdot V}{8 \cdot \pi \cdot t \cdot l \cdot \nu} \times 100$$

where m is the Hagenbach-Couette correction, V the capacity of the measuring bulb in mls., t the time of flow of the liquid in seconds, l the length of the capillary in cm., and ν the kinematic viscosity of the liquid in stokes. Assuming $m = 1{\cdot}0$, and knowing V and l, the correction can be calculated for liquids of varying viscosities; t is, of course, measured for the liquid concerned.

As the effect of kinetic energy is to give a viscosity figure higher than the true result, k in the expression $\eta = k \,.\, t \,.\, d$ must be correspondingly reduced in order to obtain correct results; a curve can thus be plotted showing the correct value of k to be used for any given time of flow. This method is very convenient where a large number of results are to be obtained using the same viscometer. (Figs. 2 and 3.)

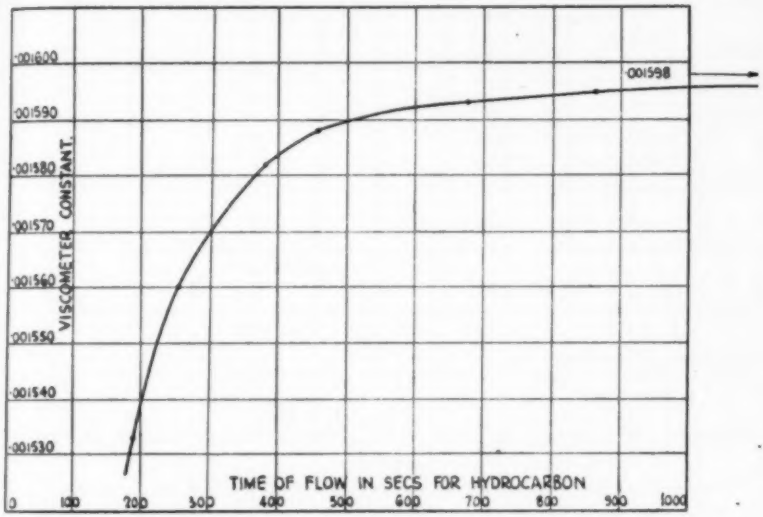

FIG. 2.

CALIBRATION CURVE FOR VISCOMETER NO. 1.

There is a considerable amount of doubt as to the correct value of m, values from 1·0 to 1·2 being employed. In cases where the Reynolds criterion is below 10, it is stated by Dorsey and others [5] that the correction is not applicable at all. However, in these viscometers the correction is kept so low that a slight variation of the value of m introduces an error so small as to be negligible, while for the liquids of viscosity high enough to bring the Reynolds number below the figure of 10, and hence into the region of doubtful applicability, the value of the correction, whether m is taken as 0 or as 1·0, is so small as to be practically negligible.

As a further check on these conclusions, however, it was thought advisable to calibrate the instruments with mercury and water and obtain a two-constant equation for the viscometers, by solving pairs of equations of the type

$$\nu = AT - B/T$$

Thus for the viscometer with 0·048-cm. diameter capillary, the equation obtained was

$$\nu = 0{\cdot}001597T - 2{\cdot}13/T.$$

Table IV shows that the agreement between the results obtained using this method of calibration and those given by using the values of k found by assuming $m = 1{\cdot}0$ are excellent. This demonstrates that the value of m taken is sufficiently accurate even for liquids of as low viscosity as 0·25 centipoise, for which the kinetic energy correction on the No. 1 viscometer is about 2½ per cent.

To ensure the absence of errors of the type experienced with the original

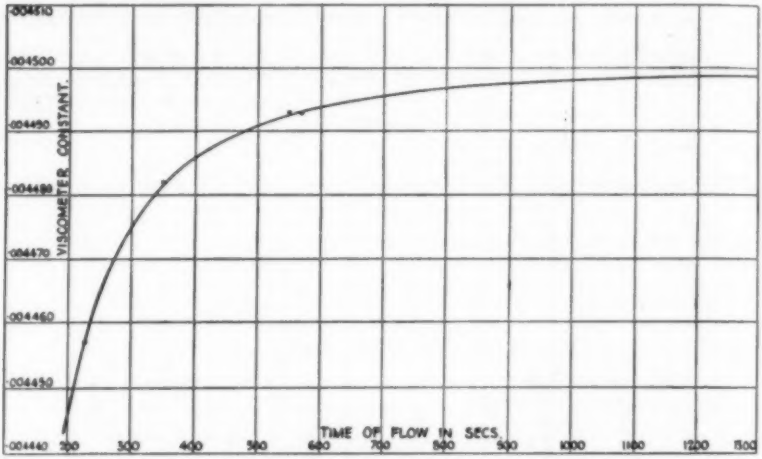

FIG. 3.

CALIBRATION CURVE FOR VISCOMETER NO. 2.

B.E.S.A. No. 1 viscometer in the determination of the viscosities of very light hydrocarbons, it is therefore worth while to calibrate an instrument with water, mercury and a light hydrocarbon such as *n*-heptane or *iso*-octane, both of which latter can be obtained in a very pure condition by treating the materials supplied as engine standards with sulphuric acid, and

TABLE IV.

Comparison of Calibration Methods.

Hydrocarbon.	Viscosity Calculated using $m = 1{\cdot}0$.	Viscosity Calculated from $\eta/d = AT - B/T$.
*iso*Octane at 20° C. . . .	0·5024 cp.	0·5022
*iso*Octane at 75° C. . . .	0·2839	0·2847
*iso*Octane at 90° C. . . .	0·2478	0·2486
*cyclo*Hexane at 15° C. . . .	1·072	1·071
*cyclo*Hexane at 75° C. . . .	0·4384	0·4398

then distilling. The viscosities of these compounds at 20° C. are 0·409 cp. for heptane and 0·503 for *iso*-octane. Using either the two-constant equation obtained by the use of mercury and water, or the method of correcting k by assuming $m = 1{\cdot}0$, the values for the hydrocarbons should be obtained with a high degree of accuracy.

A large number of measurements had previously been determined on the small-bulb viscometer, and these are higher than the true figures obtained on the correctly designed instruments. The percentage excess of the

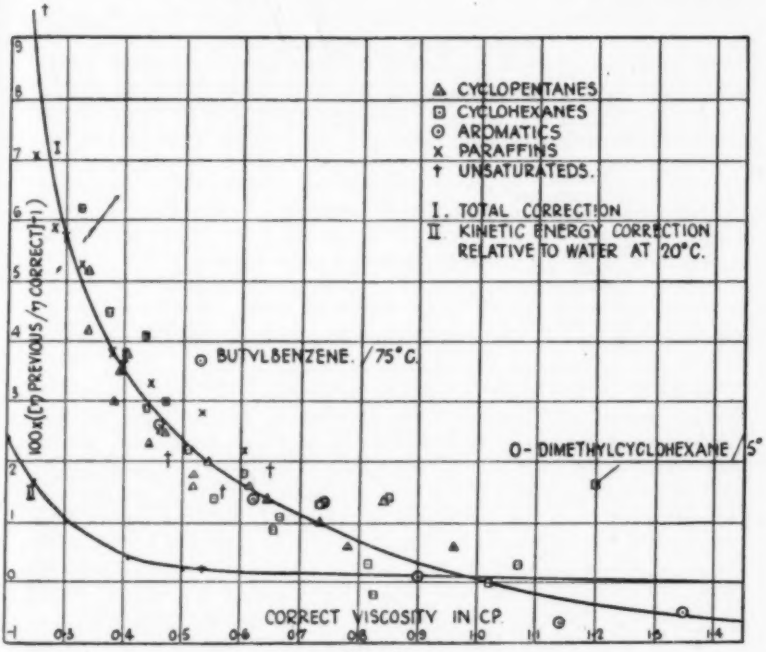

FIG. 4.

CORRECTION CURVE FOR RESULTS ON B.E.S.A. NO. 1 VISCOMETER WITH NEW CAPILLARY.

first series of results over the true viscosities are shown in Fig. 4. The kinetic energy correction curve for the small-bulb instrument, which had not been allowed for in computing the viscosities on this instrument, is also shown on the same diagram, and is seen to account for only a very small part of the total error, even at very low viscosities.

There is obvious relation between the magnitude of the error and the viscosity. The points, which represent determinations on paraffins, five- and six-membered naphthenes, aromatics and olefines, do not deviate from the mean curve by more than ½ per cent. If kinematic viscosities or time of flow in the new viscometer had been used instead of absolute viscosities in centipoises, the agreement would probably have been much closer.

In his paper (*loc. cit.*) Barr deduces from a consideration of surface tension effects that benzole should show a viscosity, measured in a small-bulb viscometer, about 1·3 per cent. lower than the true value. This result is in the opposite sense to that found in our work. Furthermore, if the surface tensions of water and various hydrocarbons be compared, as in Table V, it is seen that although the figures for hydrocarbons are much lower than for water, they differ very little among themselves. The magnitudes of the errors which we find are not at all in line with these surface tensions.

TABLE V.

Surface Tensions of Hydrocarbons, etc.

Hydrocarbon, etc.	Surface Tension, dynes/cm.
Trimethylethylene	17·3
Benzene	28·9
n-Hexane	18·5
Ethylbenzene	29·6
n-Octane	21·8
Diisoamyl	22·2
Mesitylene	28·5
*cyclo*Hexane	25·3
n-Propylbenzene	29·0
Gasoline	19–23
Kerosine	23–32
Water	72·7

Barr, in his argument, considers the discharge of liquid from a bulb having conical ends, into a cylindrical recipient, and calculates the hydrostatic head at any part of the flow on the basis of this assumption. Actually, however, the recipient bulb is very similar in shape to the measuring bulb, and when the upper level is in a conical portion of the bulb, the lower level, will probably be in the corresponding portion of the lower bulb. Even in an extreme case the lower level must rise on at least one conical surface. It would appear that the effect of capillary rise in the recipient bulb which was not considered in this reasoning is important, as actually, we consider, it would approximately neutralize the effect in the measuring bulb.

We do not consider, therefore, that the errors met with in these small viscometers are due to surface tension, as suggested by Barr, for these reasons, and particularly because the magnitude of the error is not related to the value of the surface tension for any particular hydrocarbon. The effect is probably due entirely to drainage. If the viscometer has small bulbs, the surface is relatively large compared with the volume. In the case of a liquid much thinner than the calibrating liquid, the level falls very quickly, a considerable proportion of the liquid is left behind on the walls of the bulb by drainage, and the mean head is reduced and the apparent viscosity is increased. For more viscous liquids the rate of fall of the surface is decreased, the surface tension is hardly altered, and so the drainage error becomes proportionately reduced. For liquids with viscosities approaching that of the calibrating liquid, the effect becomes very small, and may even change to a slight error in the opposite sense, owing to the large surface tension of water and comparatively large drainage showing by this liquid in consequence. There are indications of this in Fig. 4.

Experimental Details.

The apparatus used for the measurement of viscosities was of a very simple type. The bath consisted of a large glass jar, suitably lagged except on one portion, which was left uncovered to enable observations to be made. For most of the measurements the bath was filled with water, but for temperatures in the region of 100° C. and higher either ethylene glycol or a light mineral oil was employed. The glycol is more generally satisfactory up to 150° C. Stirring was by means of an electrically driven paddle, and heating was carried out by means of an electric immersion heater, in series with a variable resistance. Hand control of the resistance sufficed to maintain the temperature constant within $\pm \frac{1}{20}$° C. for an indefinite period; the same temperatures were employed for measurements on most of the compounds, and a little experiment allowed the positions of the resistance slider for various temperatures to be marked off with considerable accuracy. Minor adjustments, when necessary, were made during the experiment. This procedure was found to be very convenient in practice; far more so, in fact, than the use of a thermoregulator, since a range of about 90° C. had to be covered in intervals of 15° C. For temperatures below that of the room (*i.e.* 5° C. and 15° C.) a regulated stream of ice-water was found to give adequate temperature control.

The viscometer was fitted with cotton-wool filters to prevent ingress of dust particles, using the device recommended in the B.E.S.A. specification No. 188 of 1929. Verticality of the instrument was assured by sighting in two planes against plumb-lines suspended in the bath near to the viscometer. The viscometers were cleaned after each substance by soaking in chromic-acid mixture, washing with pure distilled water, then with filtered acetone, and dried by passage of a current of warm, dust-free air. The thermometer used was graduated in tenths of a degree centigrade and calibrated for 8 cm. immersion. Two stop-watches were used, and these were frequently checked against a synchronous electric clock.

In carrying out the determination of the viscosity–temperature curve of a given hydrocarbon, the material was first filtered into the viscometer, which was then placed in the bath adjusted to the lowest temperature to be employed (usually 5° C.). After allowing a suitable time, usually about 15 mins., for the liquid to assume the temperature of the bath, the levels of the hydrocarbon in the viscometer were adjusted using a finely drawn-out capillary. At least three concordant runs were obtained at each temperature, any irregularities observed involving the taking down and re-cleaning of the instrument. After a satisfactory observation, the bath temperature was raised to the next desired point, and, after equilibrium had been attained, the levels were adjusted once more by means of the capillary, and a further series of runs taken. In this way the whole of the determinations at 5° C., 15° C., 30° C., 45° C., 60° C., 75° C. and 90° C. were made on the hydrocarbons which were liquid at ordinary temperatures. In the case of those compounds which are solid at room temperatures, the materials were melted and filtered into the viscometer in an air-oven, the viscometer then being quickly transferred to the bath, which had been raised to a temperature above the melting point of the hydrocarbon. The adjustment of levels was made as before, and the first reading taken at a temperature

slightly above the melting point, subsequent readings being made at temperatures which were multiples of 15° C. until a suitable range had been covered. Thus in the case of naphthalene, m.p. 80° C., the readings were taken at 85° C., 90° C., 105° C., 120° C., 135° C. and 150° C.

From the calibration curves (Figs. 2 and 3) the appropriate viscometer constants for the times of flow observed were read off and multiplied by the time of flow in seconds, and the density of the hydrocarbon at the temperature of measurement (obtained by extrapolation or interpolation from the experimental determinations) to give the desired viscosity in centipoises: thus

$$\eta = k \,.\, t \,.\, d.$$

PART III.

The Viscosities of Normal Paraffins.

The normal paraffins form the best example of a homologous series of compounds, the properties varying regularly from member to member; the viscosity data form no exception in this respect.

The best series of determinations of viscosities of normal paraffins remains that of Thorpe and Rodger [6] who made measurements on *n*-pentane, *n*-hexane, *n*-heptane and *n*-octane from about 0° C. to just below the boiling point. Kuenen and Wisser [7] investigated *n*-butane over the range −23·6° C. to +34·5° C. Bartoli and Stracciati [8] recorded single determinations at temperatures varying from 21·9° C. to 24·4° C. on the normal paraffins from *n*-pentane to *n*-hexadecane. The hydrocarbons were obtained by fractionating a Pennsylvanian light oil and treating successively with concentrated sulphuric acid and fuming nitric acid. The hydrocarbons are by no means pure, containing appreciable quantities of naphthenes which are not removed by this treatment. The viscosity results are, in consequence, not accurate, as would be expected also from a consideration of the physical constants given. Shepard, Henne and Midgley [9] made measurements on the pure normal paraffins from pentane to dodecane, prepared from petroleum. These hydrocarbons were undoubtedly of a high degree of purity, but unfortunately determinations were carried out at only one temperature, 25° C. Two results on *n*-octadecane at 32° C. and 42° C. have been recorded by Dover and Hensley.[10] These determinations are, however, not in good agreement with other data, nor does the coefficient of change of density with temperature correspond with those of other members of the normal-paraffin series (d_0^{32} is given as 0·7790 and d_0^{42} as 0·7756).

Some measurements on tetradecane, hexadecane and octadecane are quoted in Engler–Höfer.[11] The normal paraffins higher than this are represented only by *n*-dodecatriacontane, the viscosity of which was determined at 75° C. and 100° C. by Delcourt.[12]

Besides these results, there are four measurements on *n*-hexane, by Bingham, White, Thomas and Caldwell,[13] which are in agreement neither with the results of Thorpe and Rodger, nor with those of Shepard, Henne and Midgley; measurements at 15° C. and 30° C. on hexane and octane by Timmermans and Martin [14] and results for *n*-heptane at 20° C. by Edgar, Calingaert and Marker [15] and at 25° C. by Lewis.[16]

Apart from these data there are also some fluidities recorded by Bingham and Fornwalt [17] which have been converted into viscosities. The measurements cover the range from 0° to 100° for nonane, decane, undecane and dodecane, and are in fair agreement with the results of Shepard, Henne and Midgley at 25° C. The viscosity of dodecane at 25° C. is about 1·5 per cent. higher than Midgley's figure and about 2·5 per cent. higher than our own.

New measurements have also been made by the author on *n*-dodecane and *n*-hexadecane. The results on *n*-hexadecane are slightly higher than those recorded by Ubbelohde and Agthe, while the result for *n*-dodecane at 25° C., given by Shepard, Henne and Midgley, is about 1 per cent. higher than the value obtained by plotting our own results.

The details of preparation and physical constants on the samples of *n*-dodecane and *n*-hexadecane used are as follows :

n-*Dodecane*. This hydrocarbon was prepared by the catalytic hydrogenation of dodecene, by the Adams platinum-black method. The dodecene was obtained from crude lauryl alcohol separated from the technical product known as "lorol," as described elsewhere in the paper. The hydrogenation went very easily, and after removal of any traces of unchanged dodecene by treatment with sulphuric acid and redistillation, the properties were as follows, comparison being made with the data of Shepard, Henne and Midgley [9] :—

	Our Data.	Shepard, Henne and Midgley.
B.p., corr. . .	216·3 ± 1° C.	216·2° C.
d_4^{20}	0·7501	—
d_4^{25}	0·7465	0·7454
d_4^{30}	0·7285	—
n_D^{15}	1·4249	—
n_D^{20}	1·4225	1·4219
A.p. . . .	83·5° C.	83·7° C.

n-*Hexadecane*. As in the case of dodecane, hexadecane was obtained by the catalytic hydrogenation of the corresponding olefine, viz. cetene. In this case also the reaction goes very smoothly, and the data compared with those of Waterman, *et al.* [18] are given below.

	Our Data.	Waterman, *et al.*
d_4^{20}	0·7752	0·7751
d_4^{30}	0·7544	—
n_D^{15}	1·4380	—
n_D^{20}	1·4358	1·4352
A.p. . . .	95·1° C.	—
M.p. . . .	16·9° C.	17·8° C.

The original data are given in Tables VI to X, while Table XI shows the selected values, in centipoises, for a number of these hydrocarbons. Table XII contains the kinematic viscosities in centistokes, together with densities

TABLE VI.

Kuenen and Wisser (1913).		Thorpe and Rodger (1895).								Bingham, White, Thomas and Caldwell (1913).		Ubbelohde and Agthe (1913).							
n-Butane.		*n*-Pentane.		*A*-Hexane.		*n*-Heptane.		*n*-Octane.		*n*-Hexane.		*n*-Tetra-decane.		*n*-Hexa-decane.		*n*-Octa-decane.	
T. ° C.	η.	T. ° C.	η.	T. ° C.	η.	T. ° C.	η.	T. ° C.	η.	T. ° C.	η.	T. ° C.	η.	T. ° C.	η.	T. ° C.	η.
−23·6	0·265	0·74	0·2605	0·80	0·3931	6·43	0·4797	0·25	0·700	25	0·3289	20	2·180	20	3·341	20	—
0·0	0·207	7·47	0·2620	9·15	0·3581	6·56	0·4795	12·18	0·594	35	0·2828	40	1·465	40	2·150	40	2·862
18·5	0·176	13·16	0·2481	14·75	0·3378	13·46	0·4418	22·92	0·520	50	0·2746	60	1·105	60	1·530	60	1·918
34·5	0·153	18·91	0·2351	19·98	0·3202	21·74	0·4027	32·96	0·463	65	0·2177	80	0·848	80	1·136	80	1·342
		26·30	0·2192	25·39	0·3035	30·27	0·3885	43·89	0·411			100	0·658	100	0·864	100	1·062
		30·41	0·2110	30·23	0·2894	38·34	0·3397	54·73	0·367								
		32·66	0·2070	36·76	0·2722	47·25	0·3112	66·46	0·328								
				43·47	0·2557	55·03	0·2890	77·82	0·296								
				47·42	0·2470	62·04	0·2714	88·33	0·269								
				52·90	0·2351	70·09	0·2526	98·52	0·247								
				58·76	0·2231	77·70	0·2372	109·07	0·227								
				63·59	0·2143	85·49	0·2218	122·07	0·204								
						92·21	0·2096										

at 0° C., 50° C. and 100° C. In a number of cases the densities have had to be obtained by plotting and comparison of isolated measurements given in the literature, since no figures are given for the actual material on which the viscosity measurements have been carried out.

TABLE VII.

Hydrocarbon.	Temp., ° C.	Visc.	Author.
n-Nonane	22·3	0·624	Bartoli and Stracciati
n-Decane	22·3	0·78	
n-Undecane	22·7	0·94	
n-Dodecane	23·3	1·15	
n-Tridecane	23·3	1·52	
n-Tetradecane	21·9	2·22	
n-Pentadecane	22·0	2·86	
n-Hexadecane	22·2	3·63	
n-Octadecane	32·0	3·557	Dover and Hensley
n-Octadecane	42·0	2·790	
n-Dodecatriacontane	75·0	6·58	Delcourt
n-Dodecatriacontane	100·0	4·09	

TABLE VIII.

Hydrocarbon.	At 15° C.	At 20° C.	At 25° C.	At 30° C.	Author.
n-Hexane	0·377	—	—	0·278	Timmermans and Martin
n-Hexane	—	—	0·2937	—	Shepard, Henne and Midgley
n-Heptane	—	—	0·3855	—	Lewis
n-Heptane	—	0·409	—	—	Edgar, Calingaert and Marker
n-Heptane	—	—	0·3859	—	Shepard, Henne and Midgley
n-Octane	0·579	—	—	0·472	Timmermans and Martin
n-Octane	—	—	0·5083	—	Shepard, Henne and Midgley
n-Pentane	—	—	0·2166	—	
n-Nonane	—	—	0·6621	—	
n-Decane	—	—	0·8527	—	
n-Undecane	—	—	1·081	—	
n-Dodecane	—	—	1·353	—	

TABLE IX.

Author's Own Data.

Hydrocarbon.	5° C.	15° C.	30° C.	45° C.	60° C.	75° C.	90° C.
n-Dodecane	1·990	1·614	1·228	0·9690	0·7861	0·6560	0·5550
		20° C.					
n-Hexadecane	—	3·522	2·782	1·995	1·567	1·248	1·017

TABLE X.

Converted Data of Bingham and Fornwalt.

Hydrocarbon.	0° C.	20° C.	25° C.	50° C.	80° C.	100° C.
n-Nonane	0·969	0·709	0·662	0·487	0·360	0·306
n-Decane	1·298	0·907	0·8405	0·601	0·452	0·357
n-Undecane	1·724	1·168	1·075	0·746	0·527	0·435
n-Dodecane	2·299	1·504	1·370	0·929	0·636	0·512

TABLE XI.

Viscosities of the Normal Paraffins.

Hydrocarbon.	Empirical Formula.	Mol. Wt.	Viscosity in cp. at					Source of Data.	Remarks.
			0° C.	20° C.	50° C.	80° C.	100° C.		
n-Butane . .	C_4H_{10}	58	0·208	0·172	0·137	(0·114)	(0·102)	Kuenen and Wisser	B.p. + 1° C. Measurements to 34°
n-Pentane . .	C_5H_{12}	72	0·282	0·231	0·1805	(0·147)	(0·130)		B.p. + 36° C.
n-Hexane . .	C_6H_{14}	86	0·398	0·319	0·2415	0·1915	(0·1675)	Thorpe and Rodger	B.p. + 69° C.
n-Heptane . .	C_7H_{16}	100	0·520	0·411	0·305	0·2335	0·1975		
n-Octane . .	C_8H_{18}	114	0·7015	0·5395	0·3845	0·2885	0·243		
n-Nonane . .	C_9H_{20}	128	0·969	0·709	0·487	0·360	0·3055	Bingham and Fornwalt	
n-Decane . .	$C_{10}H_{22}$	142	1·298	0·907	0·6015	0·4525	0·357		
n-Undecane .	$C_{11}H_{24}$	156	1·725	1·168	0·7465	0·5265	0·435		
n-Dodecane .	$C_{12}H_{26}$	170	2·239	1·466	0·9015	0·618	0·501	Author (B & F method)	
n-Tetradecane .	$C_{14}H_{30}$	198	—	2·178	1·259	0·832	0·661	Ubbelohde and Agthe	
n-Hexadecane .	$C_{16}H_{34}$	226	6·194	3·516	1·858	1·172	0·927	Author	M.p. 16·9° C.
n-Octadecane .	$C_{18}H_{38}$	254	—	4·529	2·344	1·368	1·023	Ubbelohde and Agthe	
n-Dotriacontane .	$C_{32}H_{66}$	450	—	—	—	5·945	4·09	Delcourt	

TABLE XII.

Kinematic Viscosities—N-Paraffins.

Hydrocarbon.	d_4^0.	d_4^{50}.	d_4^{100}.	Viscosity in cs. at				
				0° C.	20° C.	50° C.	80° C.	100° C.
n-Butane . . .	0·6010	0·5370	0·4730	0·3445	0·299	0·2551	(0·2285)	(0·2155)
n-Pentane . . .	0·6454	0·5892	0·5514	0·437	0·3685	0·3065	(0·2580)	(0·2355)
n-Hexane . . .	0·6760	0·6370	0·5980	0·5890	0·483	0·379	0·312	(0·280)
n-Heptane . . .	0·7000	0·6590	0·6180	0·743	0·601	0·4625	0·368	0·320
n-Octane . . .	0·7185	0·6782	0·6379	0·9765	0·7685	0·567	0·441	0·381
n-Nonane . . .	0·7325	0·6930	0·6540	1·325	0·988	0·718	0·5375	0·467
n-Decane . . .	0·7450	0·7060	0·6690	1·742	1·243	0·852	0·6615	0·5335
n-Undecane . . .	0·7550	0·7175	0·6810	2·285	1·576	1·040	0·7555	0·6390
n-Dodecane . . .	0·7644	0·7286	0·6928	2·929	1·954	1·237	0·874	0·723
n-Tetradecane . .	0·7780	0·7440	0·7075	—	2·851	1·692	1·152	0·9345
n-Hexadecane . .	0·7891	0·7544	0·7197	7·848	4·535	2·462	1·597	1·288
n-Octadecane . .	0·7960	0·7630	0·7280	—	5·769	3·072	1·844	1·406
n-Dotriacontane . .	0·8240	0·7936	0·7632	—	—	—	7·668	5·359

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DISCUSSION ON THE MICROSCOPICAL EXAMINATION OF CRUDE PETROLEUM.

THE One Hundred and Seventy-eighth General Meeting of the Institution of Petroleum Technologists was held at the Royal Society of Arts, 18, John Street, W.C.2, on Thursday, December 16th, 1937. Colonel S. J. M. Auld, O.B.E., M.C., D.Sc., President of the Institution, was in the chair.

The Secretary (Mr. S. J. ASTBURY) said he had very much pleasure in announcing that at the Council meeting held that afternoon Colonel Auld was unanimously re-elected President of the Institution for the Session 1938–39. He had also pleasure in announcing that the following gentlemen were elected Vice-Presidents: Mr. Ashley Carter, Mr. C. Dalley, Dr. F. H. Garner, Professor A. W. Nash, Mr. J. McConnell Sanders and Dr. F. B. Thole. He added that he had received a telegram which, with the President's permission, he would read, from the Roumanian Branch, which held its annual dinner on Saturday, December 11th, at Ploesti: "The Roumanian Branch sends best wishes parent Institution from their eleventh annual dinner."

The CHAIRMAN then called upon Mr. McConnell Sanders to address them on the subject of the Microscopical Examination of Crude Petroleum. He said that this paper had already been published in the September issue of the *Journal*, and that he personally was looking forward to hearing the lecturer on a subject which was almost peculiarly his own.

THE MICROSCOPICAL EXAMINATION OF CRUDE PETROLEUM.*

By J. MCCONNELL SANDERS.

BEFORE submitting his paper on "The Microscopical Examination of Crude Petroleum," Mr. McConnell Sanders said that its publication in the *Journal* last September was somewhat premature. A paper by another author was due for that month's issue, but could not be got ready in time, and since he had a great deal of material already available, he undertook to utilize this for the paper.

This meant that he had been obliged to leave out a number of items which would have made the picture more complete. On the other hand, the premature publication of the paper also meant that it had already been in the hands of members abroad, and he had had the advantage of receiving from overseas many letters and comments which had been of great value and interest to him.

Their particular value lay in the fact that they indicated that the main object of his paper had been achieved, and that was to provoke the interest

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of other workers in what he believed to be a new method of approach towards the solution of some of the problems which had been, and still were, exercising attention.

He was not presenting the paper as a solution of any of these problems, but only as a suggestion for a method which in other, and more capable hands than his own, might eventually lead to the solution.

It was for this reason that he had been at some pains to describe the methods he had employed in a very detailed manner, because only in that way could other workers see where improvement in technique could be introduced, and he had no doubt that there would be found plenty of scope for doing so.

Mr. McConnell Sanders then said that he did not intend to read the paper *in extenso*, since three months had elapsed since its publication, and he felt sure that those of the members who were interested in the subject must have already digested its contents.

He therefore proposed to contribute towards the subsequent discussion by expanding some of the salient points in the general exposition, and explaining a little more fully the reasons which lay behind some of the operations involved.

Quoting from the introductory part of the paper, he explained that the starting point of his theories was the fact that much of the information now available regarding the origin and composition of coal was obtained by the discovery of organized remains in that material, and he alluded to the important part played by the microscope in providing information relating to the nature, affinities and sometimes even of the life histories of the organized bodies which had been preserved.

From the moment that it was conceded that oil had been produced by a low-temperature process involving the decomposition of organized material, he considered that it was but a short logical step to the conclusion that, as in the case of coal, some of that material could have been preserved from total destruction, and could therefore be found in the oil.

All that was necessary to support the argument was the presence of the "aseptic enclosing material," similar to that which Stopes and Wheeler had postulated for the preservation of the remains in coal.

Mr. McConnell Sanders referred to the discoveries of Ascheim, Treibs and Hohlweg as evidence of the great preservative power of petroleum, and also to the fact that as far back as 1887 vegetable alkaloids had been reported to be present in Galician crude oil, and that free fatty acids had been found in an Indian oil from the Jaba region.

In discussing the reason for the preservative action, reference was made to the recent work of J. Risler, who had studied the bactericidal properties of essential oils and resins, and discovered that when these bodies were mixed they had a far greater preservative property than when employed singly. He alluded to the preservation of Egyptian mummies as being probably due to the use by the embalmers of mixed resins, and to the fact that some confirmation of this theory was afforded by the work of Tschirsh and Reuter, who had analysed mummies from Egypt, Carthage and Phœnicia, and had been able to identify some of these resins.

That some crude petroleum was biologically inactive had been shown by Baars, who had attempted without success to make it act as a hydrogen

acceptor or donator for sulphur bacteria. On the other hand, Baars had also shown that some of the higher fatty acids, such as had been found to exist in some Japanese crudes, could act as hydrogen donators for sulphate-reducing bacteria of the Vibrio type.

Mr. McConnell Sanders then said that one could visualize a magma of decomposing vegetable matter derived from different plants, or from different organs of the same plant, the softer cellulosic matter being attacked first with dissolution of the cementing medium and disintegration of cell-walls. Then the formation of pectic bodies and of soluble sugars which act as nutritive material for the multiplying bacteria, meanwhile essential oils and resins, liberated from the plant cells by the disintegration constituted the aseptic medium which would preserve from further decomposition those parts of the plant structure which had escaped the initial attack.

Reference was made to the pioneer work of Potonié, and to the opinion expressed by Brooks, that naturally formed hydrocarbons may have contributed to the petroleum complex, it being considered that the picture would be incomplete without also considering the waxes, and the various forms of india-rubber-like bodies. As a matter of interest, Mr. McConnell Sanders exhibited a slide of the Candelilla plant, and also a specimen of the wax which he had obtained from it, and which he had found to contain a high percentage of hentriacontane. He also dealt at some length with the existence of a large number of other plants which he had investigated, and more especially to the existence in them of terpenes and other bodies which he thought might well have contributed towards the cyclic hydrocarbons which were found in petroleum. He also discussed the significance of the undoubted presence in many types of petroleum of resins, and of the preserved remains of plant organs which still contained resins or which had originally contained them.

He also referred to the discovery of fatty acids in crudes which also contained resins, and instanced an oil from Assam which he said might have derived its content of Dammar from a dipterocarpous tree and its fatty components from the kernels of the same type of tree.

The chemical side of the investigation was then discussed with more particular reference to the mineral constituents both of the oil and of cores from producing wells.

Mr. McConnell Sanders then discussed several points in connection with his methods for conducting the microscopical examination, and explained that his fears that the form or dimensions of isolated organisms might be altered by immersion in saline solutions, or by transference from the latter to fresh water, had fortunately proved groundless.

He exhibited some lantern slides showing typical specimens of organized bodies found in samples of crude oil, and also one showing a special apparatus he had designed for the examination of objects by ultraviolet light.

He concluded by referring to a line of investigation which he thought was well worth following up, and that was the probable part taken by fungi in the genesis of petroleum, and the significance of fungal remains and spores being so frequently found in crude oil.

As a matter of interest to the present members, he also exhibited the eye-piece camera which he had devised for selective micro-photography, and

also the arrangement for taking four or six photographs on a single $2\frac{1}{2}'' \times 1\frac{5}{8}''$ plate, as an alternative to the film method which had been described in the paper.

THE CHAIRMAN said he had been entranced in listening to Mr. McConnell Sanders' talk, and no one could have listened without realizing that the research had been a labour of love. Mr. McConnell Sanders, he believed, had made all his apparatus himself, and had carried out most of his investigations with his own hands. That meant work of magnitude, combined with great assiduity, and a great deal of vision. The paper was one which, he thought, was going to be a classical reference for work of that kind. It seemed to him that fresh ground was being broken. A bridge was being built which would probably lead to knowledge which would throw far more light on the nature of the material with which they were all dealing than had been shed before.

DR. G. M. LEES said that he wished to express his great admiration for the research work of Mr. McConnell Sanders, and for the excellent presentation of the results. This line of research was something entirely new to geologists working on the elusive problem of the source of various oils. Work had hitherto been mostly confined to chemical lines of approach, and it had proved difficult to make any substantial headway. The idea had never occurred to him personally to look in the oil itself for any contained solid organic clues, but now suddenly an entirely new field of research had been opened up.

The first stage has now been passed by this demonstration that most oilfield crudes do indeed carry a sufficient amount of solid organic material to be studied, but before it will be possible to use these results for correlation purposes a formidable amount of further work is required. It will probably be easier at first to correlate one oil with another than with any given group of sedimentary rocks, in that as yet no ordinary sedimentary rocks have been searched for organisms as minute as those now under discussion. The importance of being able to define the age of a crude oil in any given area does not require emphasis. In Iran, for example, it is now thought that the oil may be of multiple source and that, in some cases, vertical migration amounting to many thousands of feet has taken place. This migration is mostly via fairly open channels through thick limestone or marlstone groups, and if these organic remains have not been filtered out in the process, an identification with original source sediments may prove to be possible. At any rate it offers a possible solution to a problem which has hitherto proved to be completely intangible. Presumably in many other oilfield areas Mr. McConnell Sanders' work will be taken up with the eagerness that it deserves, and we may look forward to important results emerging from the stimulus which he has given to oil geology.

The Chairman had said that the work had been to the author a labour of love, but it seems that Providence has rewarded him very suitably, in that his eyesight, which had been failing some years ago, had been completely restored by this intensive microscope work.

MR. J. SIMPSON (The Imperial Institute) stated that in work on coal he

had extracted bodies similar to those figured in Plates 5, 7, 8 and 12, as well as in the general plates. He would be glad to have information as to the precise size, in microns, of those spores on Plates 7, 8 and 12, which bore a striking resemblance to some obtained from coal seams in Northumberland. This similarity, if established, might indicate a definite relation between the initial vegetable débris from which coal and, apparently, oil have been derived.

Mr. McConnell Sanders said he could not give the information without referring to his laboratory note-book. The magnification given was substantially accurate, and this, taken in conjunction with the printer's note regarding the amount of reduction, would give the required dimensions.

The Chairman moved a very hearty vote of thanks to Mr. McConnell Sanders for his very interesting address, which, as he had said before, was going to be a definite landmark in the question.

The vote was carried by acclamation.

Mr. McConnell Sanders, in reply, said he would feel that they were really interested in the subject if they would write and ask him for more information, which was always at their service.

DISCUSSION ON DEWAXING.*

By V. A. Kalichevsky and R. Lee

(Socony-Vacuum General Laboratories).

"*The Principles of Solvent Dewaxing.*" By M. Ba Thi, B.Sc., A.I.C., L. C. Strang, Ph.D., T. G. Hunter, B.Sc., A.R.T.C., A.I.C., and A. W. Nash,† M.Sc., M.I.Chem.E., M.I.Mech.E.

The paper presents an attempt to utilize triangular diagrams for answering the numerous problems which are encountered in solvent dewaxing. In constructing these diagrams the wax is regarded throughout as if it were a single component which, although theoretically incorrect, is believed by the authors to be permissible for practical purposes. It would be of interest if a certain amount of experimental data were submitted to substantiate this assumption for a variety of petroleum oils.

With reference to the diagram facing page 234 in the first part of the paper and partly reproduced on page 721 of the second part, which might be considered as the basic one, it might be noted that the average melting point of the oil-free wax separated from a wax-bearing oil varies with the degree of dewaxing, and thus with the pour point of the dewaxed oil. This is illustrated by the following typical data for a Pennsylvania lubricating oil distillate of 33·0°A.P.I. gravity, 365° F. flash point, 80° F. pour test, and 96·3 Saybolt Universal seconds at 100° F.

Dewaxed Oil.		Wax.	
Pour Point, ° F.	Ultimate Yield, % Vol.	Melting Point, ° F.	Ultimate Yield, % Vol.
25	87·2	122·5	12·8
20	85·9	120·2	14·1
10	84·1	117·5	15·9
0	82·6	115·8	17·4
−10	81·3	114·3	18·7

In constructing a triangular diagram of the recommended type it is, therefore, not quite evident what melting point to ascribe to the wax which represents the " bulk " of the wax component of the wax-bearing oil.

Since the melting point of the oil-free wax varies greatly with the degree of dewaxing, the wax–oil melting-point relationships can only be represented as a family of curves, one for each condition of dewaxing as determined by the pour point of the oil. When only one wax–oil melting-point

* This contribution to the Discussion on Dewaxing was received too late for inclusion in the December *Journal*, in which the remainder of the Discussion was published.

† *J.I.P.T.*, 1937, **23**, 226–52, 707–22.

curve is used, the melting point of the wax–oil mixture obtained in dewaxing is not indicative of the true oil content of the wax. Thus, in the case of the above-mentioned Pennsylvania distillate, a 114·3° F. melting-point wax might represent either an oil-free wax obtained by dewaxing the oil to a —10° F. pour test or a wax–oil mixture containing about 27 per cent. of oil and 73 per cent. of 122·5° F. melting-point wax obtained by dewaxing the oil to a 25° F. pour test. The two products are obviously quite different, although their melting points appear identical.

The oil–wax pour-point curve likewise should be obtained by quantitative dewaxings at progressively lower temperatures, and not by blending an " average " wax with the dewaxed oil.

The above considerations indicate that the oil investigated by the authors might be considered an exception rather than a normal product, which enabled them to use the triangular diagrams for expressing the desired relationships in a comprehensive manner.

In practice the important data for dewaxing and processing purposes include the yield of a given pour-point oil and the corresponding melting point of the wax, per cent. oil in the wax cake, and per cent. solvent in the wax cake and in the filtrate. These data can be obtained experimentally with no more difficulty than those required for constructing the triangular diagrams, but have the advantage of eliminating the unavoidable assumptions which are always necessary when indirect methods are employed. The use of the indirect methods may also lead to the errors arising from the changes in the nature of the stocks which frequently occur in commercial practice.

The triangular diagrams developed in the article cover a range of oils having pour points of about 30° F. or higher. These pour points are above the usual commercial ranges, which may partly explain the results obtained by the authors. It would be, therefore, of interest to compare the observed and calculated data for the normal pour-point ranges, such as from 0–20° F., where the presence of low-melting-point waxes in an oil becomes of considerable importance in practical problems. However, even within the ranges investigated by the authors, the difference between some of the observed and calculated values for the yield of the dewaxed oil, as shown in Table II of the first part of the paper, are as high as 6 per cent., which is considerably above the permissible limits of error for data that would be of commercial value.

" *Dewaxing with Heavy Solvents.*" By Dr. Bruno Engel.*

The paper gives a very interesting summary of our present knowledge on dewaxing oils with heavy chlorinated solvents, and enumerates the various practical methods for improving the plant operating efficiencies. These methods, such as addition of small quantities of pour-point depressants or double centrifuging, are applicable to centrifuge dewaxing with other solvents than the chlorinated ones, including naphtha, but they are employed to a greater extent with more expensive solvents in order to demonstrate still further the advantage of these new processes over the conventional naphtha dewaxing methods which, as a general rule, are

* *J.I.P.T.*, 1937, **23**, 723–33.

operated without introducing the up-to-date improvements in the dewaxing technique.

The author states that with most solvents addition of synthetic oils as dewaxing aids results either in an increase in yield or in an improved pour test of the resulting product, while with chlorinated solvents this results in an improvement of both the yield and the pour point of the dewaxed oil. This is, apparently, due to the retention by the oil dewaxed with chlorinated solvents of at least some of the synthetic inhibitor. Similar results, therefore, might be expected also with other than chlorinated solvents, provided relatively large quantities of such inhibitors are added to the oil before centrifuging, or additional quantities of the inhibitor are added to the dewaxed oil. It would be therefore of interest to know whether, in the experiments conducted by the author, the quantity of inhibitor added to the oil was kept at the very minimum which is required for improving the yield of the oil and, if so, how this quantity compares with a similar quantity required to improve the yield of the oil from other processes, such as in naphtha centrifuging.

For better visualization of the results obtained by the author, it would be also of interest to know what method was employed to obtain the dewaxing data given in Tables II–IX, inclusive, because in the third paragraph of page 733 the author leads to the belief that the method was not a centrifugal one.

"*The Influence of Certain Substances on the Separation of Paraffin Wax from Oil in a Dewaxing Process.*" By E. C. H. Kolvoort, F. R. Moser and C. G. Verver.*

The authors present a highly interesting comparison of the properties of progressive wax fractions from various types of crudes which adds valuable information to our present scanty knowledge of the constitution of petroleum waxes. Although some of the new theories attempt to explain the difference between the crystalline and non-crystalline waxes only by the presence of inhibitors in the non-crystalline waxes, such explanations do not seem to be always satisfactory. This does not preclude the possibility that the presence of certain substances may modify the crystal structure of the waxes, but only implies that the different waxes are not necessarily uniform with respect to their basic structure. The inherent property of oil retention by some types of waxes investigated by the author clearly shows that waxes may differ widely in their characteristics even after they are freed from the so-called natural inhibitors.

It would be of interest if in their future work the authors investigate the effect of dewaxing "dopes" on the stocks which they employed in their analytical studies, particularly on the Roumanian crude waxy distillates.

In connection with the materials removed by recrystallizing the waxes from 50/50 methyl ethyl ketone–benzol blends at −27° C., our experience indicates that the pour point of the oil increases with a decrease in the amount of oil extracted under a given set of experimental conditions. Since this is somewhat in contradiction with the results obtained by the authors, it would be of interest to demonstrate whether the waxes they investigated differ in this respect from other types of crudes.

* *J.I.P.T.*, 1937, **23**, 734–45.

"*Methyl Normal-Butyl Ketone as a Dewaxing Solvent.*" By O. S. Pokorny and R. K. Stratford.*

Solvents which are suitable for dewaxing petroleum oils may be either single solvents or mixed solvents. The solvent characteristics of the first type of solvents are determined by their chemical structure and are invariable, while those of the second type of solvents can be altered by adjusting the relative quantities of the two or more solvent components of the dewaxing mixture. Proper comparisons between the solvents of the first and second type can, therefore, be made only after a thorough investigation of the effect of changing the solvent composition in the solvents of the second type on the dewaxing characteristics of reference oils, which has not been done by the authors.

The experimental data presented in the paper are sufficiently indicative for reaching conclusions that of the various aliphatic ketones mentioned the methyl *n*-butyl ketone is to be preferred for dewaxing purposes as a single solvent, and that this ketone may be a better solvent than trichloroethylene or propane. However, the choice of a 50/50 methyl ethyl ketone–benzol mixture for comparison of the dewaxing characteristics of this ketone with those of mixed solvents is not substantiated by sufficient experimental evidence that a better mixture of a similar type is not available. Substitution of toluol for benzol, which is a common plant practice, has, for instance, a considerable effect on lowering the miscibility temperatures, while the quantity of methyl ethyl ketone in the dewaxing mixture may apparently be reduced considerably below 50 per cent. without adversely affecting the dewaxing results, but also improving the miscibility relationships. For this reason, although the paper gives very interesting information concerning the dewaxing characteristics of methyl *n*-butyl ketone, no definite conclusions can be reached with respect to its relative value in comparison with mixed solvents employed in some of the important commercial dewaxing processes.

* *J.I.P.T.*, 1937, **23**, 746–50.

ROUMANIAN BRANCH.

ELEVENTH ANNUAL DINNER.

THE Eleventh Annual Dinner of the Roumanian Branch of the Institution of Petroleum Technologists was held at the Piccadilly Restaurant, Ploesti, on December 11th, 1937, Mr. E. C. Masterson occupying the Chair.

There was a record attendance, 89 members and guests being present. Telegrams with Greetings from Mr. Chaillet, a Past-Chairman of the Branch, and from the Parent Institution were read by the Chairman, and it was unanimously decided to telegraph best wishes in reply.

The toast " H.M. The King of Roumania " having been loyally honoured, the toast of " Our Guests " was proposed by Mr. WILLIAM BOLTON and replied to by Mr. Jos. G. DUQUE.

"THE PETROLEUM INDUSTRY OF ROUMANIA."

Mr. GWYN ELIAS, in proposing the toast of " The Petroleum Industry of Roumania," said : Tradition has determined that when proposing this toast, it should be made the occasion of a brief survey of the current position in this industry.

As most of you are petroleum technologists, I will refer first of all to technical progress throughout the past year.

In drilling, the most important development has been further progress in the knowledge and use of drilling muds, but only by drilling specialists can the importance of this problem be appreciated.

There has been a large extension of the method of well-completion, consisting of the use of a blank cemented liner which is afterwards perforated opposite the best oilsands, the most satisfactory way of selecting good sands from bad.

More spectacular progress has been made in the producing branch. Previous confidence in the ability to produce deep wells yielding very paraffinous crude has been further justified by the putting on the beam of some of the deep wells in the Boldeşti-Harsa field. Extension of this success has been limited by the inability of providing sufficient suitable equipment, owing to import restrictions.

During the last year or two repressuring operations have taken place on a modest scale, but not everyone is yet convinced of the economic success of such operations.

The local Branch of the Institution was fortunate in having two excellent papers on these two production subjects during the past session.

But undoubtedly the most important progress in the fields here is revealed in the steps taken towards more rational exploitation of the

producing sands. Preliminary steps in this direction were taken some years ago, when companies began to make spacing agreements, these being followed by partial or total closing in of wells with high gas–oil ratios. The next step taken was at Cucşani, where, as you know, conservation measures were put in hand, but, as is to be expected from an initial attempt, we did not have a full measure of success. At the present moment steps towards conservation on a bigger scale have been made at Tintea, where wells producing from the Meotic are producing only a fraction of their potential, and the agreement now being drawn up by the companies together with the State Mining Authorities will ensure that ample measures towards conservation will be taken. This, together with an agreement of Unit Operation in another area, opens up a new era of the utmost importance for the industry. It is most gratifying to see the increasing co-operation between companies displacing the old feeling of suspicion, and even mistrust, which used to be so prevalent.

So much for production; but mechanical engineers have not remained behind their petroleum colleagues, this year having shown great progress in steam installations in the fields, and improved methods of pipe-line construction.

Before leaving the question of progress in the fields, I know I am expressing the thoughts of oilfield engineers when I say how much we appreciate working with the State mining officials. While naturally putting the interests of the State first, yet at the same time they show an appreciation of the difficulties and problems confronting the operators, and they do all they can to overcome these difficulties, contributing in a large measure to the progress which we are able to record.

Refinery engineers and chemists, with refreshing modesty, inform me that they are really on their toes, and that important developments are on hand in their own section of the industry. Further replacements of the old-type shell stills by modern pipe-still installations have taken place, but it is in the direction of cracking that the greatest change is noted. Cracking in general has been a far less attractive operation because of the large increase in the price of the raw charging stock. During the past year this has risen to ten times the previous price, making the raw stock for cracking prohibitive. The fall in price of benzine has further accentuated the situation. The industry therefore, especially in view of the reduction in production, looks for other charging stock, and the present activity of all refiners is directed towards the better utilization of the light hydrocarbons (propane and butane) in the natural gas, which to-day are generally wasted. This is being effected by either the pyrolysis of these fractions, followed by polymerization or the catalytic dehydrogenation of butane, followed by polymerization to give light anti-knock blending products. The need for high anti-knock aviation fuels for both military and civil aviation uses leads this process to selective polymerization, followed by hydrogenation to give *iso*-octane for blending to yield 100 octane fuels, or even higher with the addition of tetraethyl-lead. It is in this direction that most refining companies are turning, and it is probable that future expansion of refining will be along these lines.

The question of supply of materials and equipment necessary to the industry is still unsatisfactory, owing to the import restrictions. Local

industries have done little, as yet, to meet the requirements of the oil industry, so it appears that most oil companies are developing their own workshops, but it is surely unfortunate that circumstances should force on one a policy leading towards self-sufficiency. In any case, local industries should only for the moment, concentrate on such things as tool-joints, sucker rods, etc., for which there is a constant and large demand.

In leaving the question of technical progress, I would like to mention that such progress is only possible with the help and advice given by those gentlemen who represent manufacturers and suppliers.

Turning now to the general position, it is probable that the position to-day is better than at the time of our last dinner. Exploration has on its debit side the Margineni field, which is a deep disappointment. Still inconclusive (and therefore to be left for the moment in the current account) is Mănești; so far the three wells drilled have discovered only gas, but are all probably axial locations, so that some more work must be done here before we can be satisfied. On the credit side we have Păulesti (the western extension of Boldești), the Meotic sands of Tintea and some promise of Păcureți.

It is difficult to obtain data on geophysical activity, but I have the impression that it is reduced. This is serious, and can only be due to the insufficient rewards for these very costly operations.

A serious position for the industry arises from the fall in production, synchronizing with an increase in drilling activity. Taking the first ten months of this year, we find a production of only 6 million tons, as compared with a production of 7,327,000 tons for the corresponding period of last year, showing a drop this year of 18 per cent.; and in drilling, for the same periods, 330,000 metres this year, compared with 272,560 metres last year, an increase of 21 per cent. Other things being equal, this means an important increase in the overall cost of obtaining a ton of oil. But other things are not equal; actually the above increase in the overall cost is accentuated by three things; the proportion of mechanically lifted oil in the 1937 period is necessarily higher than in 1936, the weighted average cost of materials used by the industry show an increase of 37·6 per cent., and labour costs have increased.

If we bear these facts in mind, and also look at the world oil situation, we find that during the first seven months of this year (these being the latest figures available) Roumania's contribution to the oil production of the world was only 2·67 per cent. of the total, compared with 3·61 per cent. for the corresponding period of 1936, and at the same time internal consumption has increased by 5 per cent., so that Roumania's influence in the world petroleum market is reduced. Coupled with this, production in the United States during the first nine months of 1937 is up by 18·4 per cent. on the corresponding period of 1936, and throughout the present year has been consistently above the figure recommended by the U.S. Bureau of Mines.

From February 1936 to September of this year there has been a persistent increase in United States production, and crude oil stocks have increased by 8 per cent. At first sight this increase might appear to be small, until we remember that only a small surplus in supply over requirements can play havoc with prices. It would also appear that there has

been some setback to industrial activity in America, and this might soon result in a demand for petroleum products below that which has been hitherto estimated. Now, if to this situation you add the fact that a month ago Constantza f.o.b. prices were, on the average, 37 per cent. higher than Gulf prices, you will appreciate that the position of the Roumanian petroleum industry is precarious. And we technical men can do little or nothing to meet this. The situation which might conceivably arise can only be met by action of the State. When you consider that 25 per cent. of the income of the State and 25 per cent. of the income of the State Railways are derived from the petroleum industry, you have to hope that the Government will realize the situation and take those steps which lie in its power to preserve, not only the industry, but also the coincident interests of the nation.

So far there are no signs of such action. I wonder can it be that, although production has declined, yet the higher prices which have been ruling—resulting in a bigger income—have brought about a false sense of security? What other explanation can there be for the recent threat to mulct the industry of an additional 470 million lei annually for C.F.R. freights? Is this an original way of wishing one a happy and prosperous New Year? If so, no wonder people speak of the good old times.

Of course, it is much easier to demand a few additional hundreds of millions of lei rather than take steps to reduce expenditure, as the industry is constantly having to do (in spite of the fact that the solution to the problem is not too difficult—namely, a pipe-line to Constantza).

Before drinking the health of the Roumanian Petroleum Industry, we should look for a moment at the possibilities for improving the position of the industry in the future.

First place must be given to the question of future production, which is a function of exploration work. The new mining law provides extended measures for exploration, over and above the possibilities which existed under the old laws, but so far no practical change has taken place, and the future sources of production are still virtually unknown. The industry is at a loss to explain the attitude of the Government towards exploration. After all, a more definite knowledge of reserves would enable the State to programme accordingly, and thereby eliminate one of the unknowns of future budgets. Machinery has been provided by legislation, whereby the rate of development of future reserves is at the will of the State, so there is not the danger that rapid exploration would result in too rapid exploitation. A further reason for accelerating exploration is that, as the industry has to bear the cost, it might not be willing to meet such heavy expenditure at a time when income is reduced by declining production.

If exploration results in oil being found in such distant parts as Transylvania, Moldova or Oltenia, there might be quite a problem in raising the capital necessary for the tremendous investment which will be involved, and the industry might do well to prepare for such an eventuality.

Turning from exploration, which is the key to the future of the industry, to questions of rather lesser importance, we find other steps which could well be taken. It is a cause of astonishment to engineers that gas is wasted within a few miles of where we are now. Yet Bucarest, 35 miles away, the semi-industrial Prahova Valley and the important industrial

town of Brașov are without natural gas, with the exception of Ploesti and Campina. A neighbour, Poland, has shown the way towards the use of natural gas by piping it for distances unheard of in this country.

Another neighbour, Jugo-Slavia, has adopted a measure which is certain to be fruitful. There they have recently made important tariff reductions on benzine, diesel oil and lubricating oils—in other words, just those products which are used by motor vehicles. At the same time consumption taxes (*i.e.* State, district and town together) are being reduced by nearly 40 per cent. Not content with this, the duty on motor vehicles has been reduced from 30 to 15 per cent. ad valorem. The policy is most courageous, and is bound to have a tremendous influence on the use of motor vehicles. At the same time it is a very shrewd move, which will ensure a big increase in the number of vehicles available in the country at times of national emergency. This must be particularly important in a country which has no motor industry to produce vehicles when the usual sources of supply are cut off. Here there is one motor vehicle to more than 500 inhabitants, so that compared with more European countries we are virtually "unmotorized."

Coupled with this question is the long-standing one of roads. A very small proportion of the country's roads are very good, nearly all the rest are very bad. Only a few days ago a truck on the main road between the two important towns of Ploesti and Târgoviște became so hopelessly bogged in the *middle of the road* that it was necessary to unload it to free it. Look at the impetus given to motoring by the good road from Giurgiu to Oradea Mare. What a sum this must have yielded in taxes on benzine alone! And as one sees an ever-increasing number of diesel-engined vehicles on the road, we must see to it that sufficient filling-stations and depôts are equipped for supplying the necessary fuel; already we are much better off than many countries, but the demand is increasing from day to day.

These are a few measures which could be taken for the betterment of the industry, and if you think of each one in turn, there is not one which would not be of real value to the nation itself.

The country has as Minister of Industry and Commerce a gentleman who deservedly has the reputation of a great industrialist, one to whom we look to harmonize the interests of the State and the Petroleum Industry, interests which at their core are indistinguishable, and so it is with optimism that I propose to you, Mr. Chairman and Gentleman, the Toast of "The Roumanian Petroleum Industry."

The DIRECTOR-GENERAL OF MINES, MR. TZANTZAREANU, replied to the toast.

PROF. THEODOR FICSINESCU proposed the toast of "The Institution of Petroleum Technologists," and MR. PERCY R. CLARK in reply referred to the growth of the Institution throughout the world, and said that since the inauguration of the Roumanian Branch over 50 papers had been read to this Section dealing with various aspects of the Petroleum Industry. He referred to the former timidity on the part of certain of the big oil concerns in allowing members of their staffs to read papers before the Institution.

Most people felt that they had some special exclusive knowledge, but the sum total of an individual's knowledge compared to the sum total of human knowledge was as the proverbial drop of water to the ocean. If twenty or thirty specialists in one branch of activity pooled their knowledge, all would undoubtedly know much more of the subject than they did before. He thought that in the reading of a paper before an audience, the lecturer learnt more from his paper than anyone in the company listening to him.

One could say that one of the leading features of twentieth-century life was the development of the conference system. Representatives of professions, industries and sciences were gathered together into societies for the pooling and increase of their knowledge; professional men, employers and employees were formed into federations to further their interests and protect their rights; businesses were largely managed by committees of members of the Company's staff.

Experience seemed to be showing that this trend was the right one from every point of view and he thought that they should do all they could to foster that co-operative spirit.

AN INVESTIGATION INTO THE COST OF OIL ABSORPTION PLANT FOR NATURAL GASOLINE RECOVERY AT HIGH PRESSURE AND LOW TEMPERATURE.*

By A. H. Nissan, B.Sc. (Stud. Inst.P.T.).

Synopsis.

One of the most important methods for gasoline recovery from natural gas is the oil-absorption process. The amount of gasoline absorbed by the oil in such a process varies with the operating pressure and temperature.

In this paper a concrete case is considered in which a reasonable composition for the initial gas and final product is assumed. A series of absorption plants operating under pressures from 1 to 6 atmospheres at a constant temperature of 30° C. have been designed. Operating conditions are thus investigated for varying pressures and constant temperature. Another series of absorption plants working under a constant pressure of 1 atmosphere but at temperatures varying from − 10° C. to 30° C. were then designed to study the effects of varying temperatures.

Costing of the resulting eight different designs has been attempted on a comparative basis. All capital costs for the various compression and refrigeration systems have been plotted. Operating costs have been similarly plotted.

Finally, from the information so obtained, a choice has been made of the most economic system. The paper is entirely comparative in character and no great importance must be attached to the actual figures, but only to their comparative values.

Introduction.

The purpose of this paper is to study the effect of varying operating temperatures and pressures on the cost of recovering gasoline from natural gas by an oil-absorption process. It is not necessarily assumed that an oil-absorption process is the most economical method of natural gasoline recovery. The method of attack being followed here is to take a definite and typical case and design the plant (1) varying the pressure but keeping the temperature constant, (2) varying the working temperature and keeping the pressure constant for the absorption column of the different plants. Thus we shall have a number of similar plants, all accomplishing practically the same results, but each differing from the rest in the dimensions of its major parts and the amount of working fluids necessary, and hence in its cost. We can then obtain curves showing the total costs for each of the plants thus designed, from which curves the most economical working conditions can be found.

The methods and principles of design employed here are the standard methods well discussed in the literature. No attempt at innovation has

* For this thesis the Author was awarded the Student's Medal and the Burgess Prize, 1937.

been made except in minor cases. Thus we shall have no excursions into the theory behind the graphical and some of the empirical methods employed, nor enter into a controversy about the fundamental assumptions being made at the start of practically every mathematical derivation of the formulæ used hereafter. Reference will be made to those methods, conceptions or formulæ which the author considers as not being found in the more common books, but only in articles recently published.

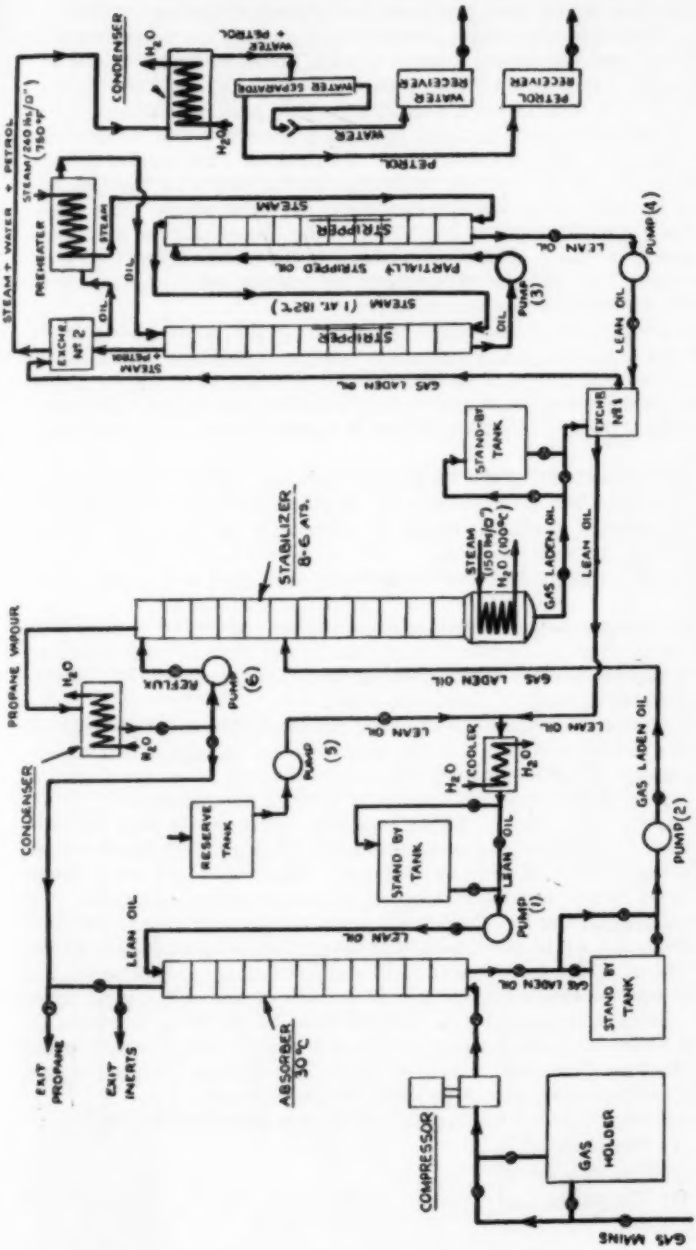
As the error in the total cost estimate of each of the different plants need not be less than about 10 per cent. to give a fairly good comparative value, it was decided to ignore the details in the design of any major component—such details as the special forms of bubble caps and intercoolers in the absorber to extract the heat of absorption, etc. However, it must be borne in mind that after choosing any one system, or combination of systems, as being the most economical, these details become important, and their cost estimate essential in the final estimate. Only by careful design of the smallest detail can the most economical means of recovering the natural gasoline desired be arrived at.

Generally speaking, the gas is scrubbed countercurrently in an absorber of the bubble-plate type, and leaves " dry " at the top. The rich oil is rid of practically all its contents of propane in a stabilizer, and then the natural gasoline is stripped by live steam from the oil. The lean oil is recirculated again. The steam and gasoline are then condensed and separated.

Referring to Fig. 1, the " compression absorption " plant will be described in greater detail. The natural gas collected by field lines can be delivered directly to a compressor (or into a holder, and then to the compressor, in order to regulate the rate of gas flow). The compressor is provided with interstage coolers, and an external one too, in order that the exit temperature of the gas is always 30° C. for all the different plants working under compression. Thus, while the temperature of the gas entering the absorber is 30° C. in all cases, the working pressure will be 1 atm., 2 atms., 4 atms. or 6 atms.—1 atm. being considered 15 lb./sq. in. throughout. The gas flows in the absorber upwards, passing through bubble plates of the ordinary type. The lean oil, having come at the beginning from the reserve tank through a cooler, is pumped to the top of the absorption column and thus flows countercurrently to the gas, absorbing propane, butane and the higher hydrocarbons.

The rich oil is then pumped to approximately the middle portion of the stabilizer. At the bottom of the stabilizer, which it reaches by gravity, it is heated by steam without coming into contact with it. The stabilizer is designed to work under pressure so that only the lighter propane and very little butane are vaporized. The pressure in the stabilizer is controlled by a valve on the vapour outlet in the condenser near its top. The condenser will thus contain propane under pressure both in the liquid and vapour phase. The liquid propane is refluxed into the stabilizer, while the vapour is taken out through the exit. It can be taken either through an independent line or mixed after pressure reduction with the " inerts,"—the dry gas from the exit of the absorber.

The rich oil from the bottom of the kettle, which is heated and stabilized for propane content, is now on its way to the stripper. It passes through a



COMPRESSION ABSORPTION

FIG. 1.

heat exchanger, taking away heat from the stripped oil coming out from the stripper; then through another, abstracting heat from the vapours arising from the stripper, and finally through a steam preheater before it falls into the stripper. Superheated steam is passed through the preheater heating the rich oil and then through a reducing valve, and is admitted at the bottom of the stripper. The steam and rich oil thus flow countercurrently, and the contents of the oil are stripped. The lean oil, after passing through the heat exchanger to heat the incoming rich oil, and thus itself cooling down, is further cooled (30° C.), and starts the cycle again. The steam and petrol vapours are partly condensed in the heat exchanger mentioned above, and then totally condensed in a bank of condensers before they go to a separator. The water is taken from the bottom, while the recovered gasoline is drawn from the top and stored.

Tanks are provided in the circuit in such a way that a breakdown in one part of the apparatus will not result in flooding the others, but while the oil is in its normal travel, these tanks are by-passed, and should be empty.

It was considered more economical to put the stabilizer where it is, instead of after the stripper (which latter case is usually followed), for two main reasons :

(1) The temperature of the oil and petrol in the stripper is higher than that in the stabilizer, thus, putting the stabilizer before the stripper, conserves the amount of heat necessary by allowing a better chance for heat exchangers to be used efficiently. This is especially the case with the " refrigeration absorption " process working at 1 atm. and reduced temperatures.

(2) The propane being stripped in the stabilizer will no longer need to be heated to the high temperature employed in the stripper and cooled, as would be necessary in the other arrangement. Thus there will be a further economy in the amount of steam consumed.

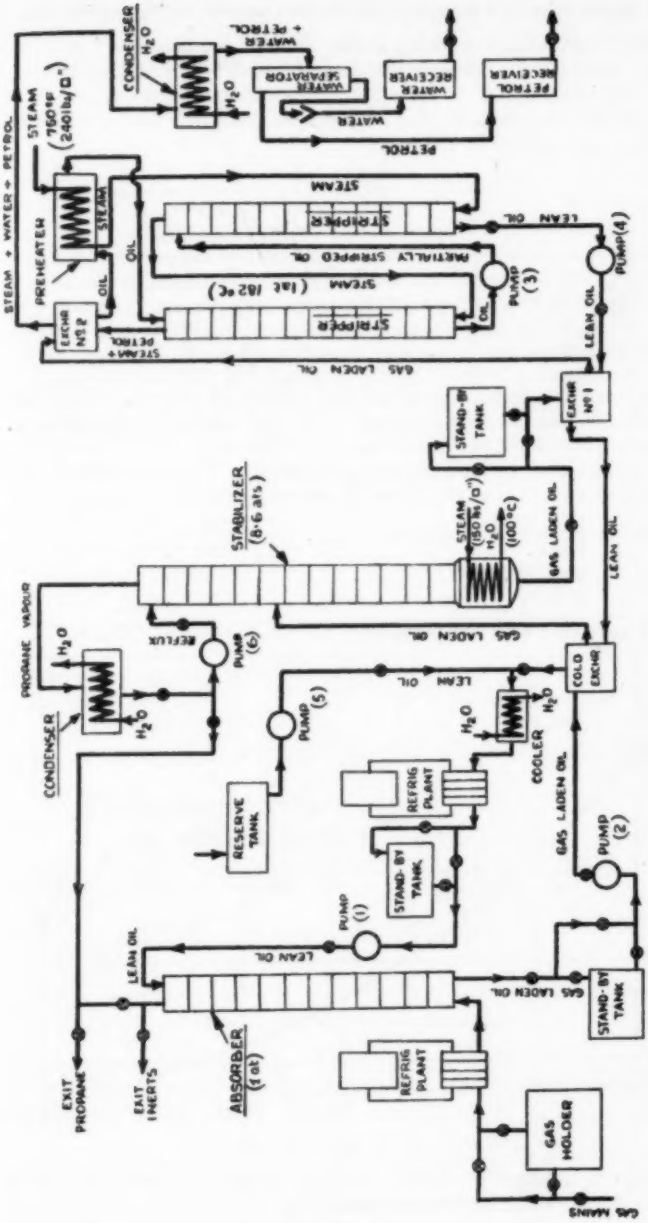
In the refrigeration absorption process practically the same procedure is followed. The gas is collected in the same way, but is refrigerated instead of compressed. The working pressure in the absorber is always 1 atm. or 15 lbs./sq. in., while designs are made for working temperatures of 30° C., 20° C., 10° C., 0° C. and — 10° C. Another difference is that the rich oil is pumped through a heat exchanger before its entrance to the stabilizer, thus cooling the lean oil from the stripper. This cooled lean oil is further cooled down by a refrigerating component before it resumes its cycle. The rest, as will appear from Fig. 2, is the same as the compression absorption plant.

An advantage can be taken here from the compressed propane gas leaving the stabilizer. This, on a further slight compression, is easily liquefied, and could be used as the refrigerating fluid in both or one of the components cooling the oil and natural gas. But as refrigerators using ammonia are more of a standard, the increase in cost of a special design using propane might offset the advantage. As no special innovation was being attempted, the usual refrigerating apparatus would be incorporated.

It is apparent that the whole plant can be split into three major parts :

(1) The absorber.
(2) The stabilizer.
(3) The stripper,

and a fourth



REFRIGERATION ABSORPTION

FIG. 2.

(4) Accessories like pumps, compressors, coolers, refrigerators, etc.

Again each part will be working under either " compression " or " refrigeration " conditions. Thus we will deal with each major part separately, firstly for compression and secondly for refrigeration absorption.

Our Assumptions.—Assume that the gas to the plant has a constant composition, as tabulated in Table I.

TABLE I.

Component.	Volume, %.	Mol. Comp. / Mol. Inerts.
CH_4	50·0	Inerts
C_2H_6	30·7	Inerts
C_3H_8	13·5	0·167
nC_4H_{10}	4·2	0·052
C_5H_{12} +	1·6	0·0198

" Inerts " are the gases which are not soluble in the oil. Thus any nitrogen, etc., will be returned as a part of the methane and ethane present. The gas rate of flow to the plant is constant at 5,000,000 cu. ft./day available at a pressure of 1 atm. and a temperature of 30° C. We will scrub this gas with a Shell Mex Gas Oil of the following characteristics :

Mol. Wt.	200
I.B.P.	220° C.
50% Pt.	250° C.
F.B.P.	320° C.

Its density variation with temperature is shown in Table II (Fig. 3).

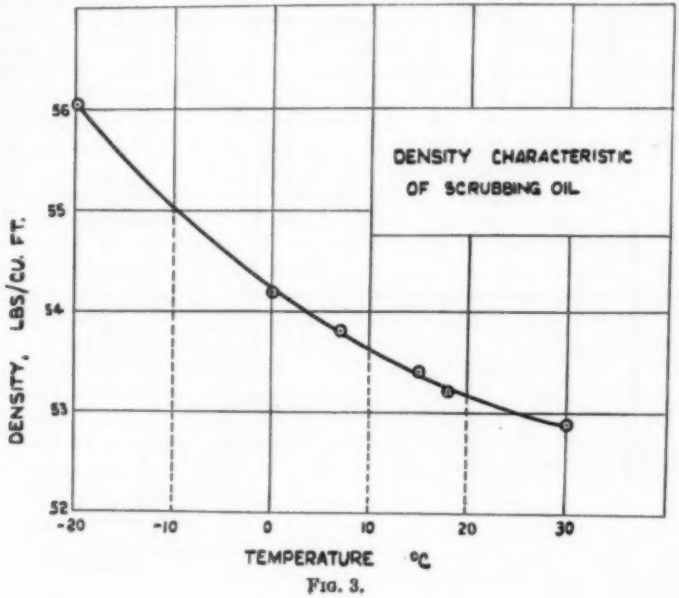


FIG. 3.

TABLE II.

Temp., ° C.	Density, kg./m.³	Density, lbs./cu. ft.
30	845·4	52·9
18	851·8	53·2
15	853·3	53·4
7	861·2	53·8
0	867·3	54·2
−20	897·3	56·1

This oil was chosen to fulfil the conditions that make it a good scrubbing oil : its initial boiling-point is well above the end point of the gasoline, it is light and has low cold test and no great tendency to emulsify, while its viscosity is not so great as to make its handling expensive.

It is required to find the effect of varying operating temperatures and pressures on the cost of recovering by oil absorption exactly 80 per cent. of the total butane in the gas, together with as much of the " pentane plus " and as little of the other constituents as possible.

THE ABSORBER.

1. *Compression.*

This was designed by the usual graphical method shown in Fig. 4.

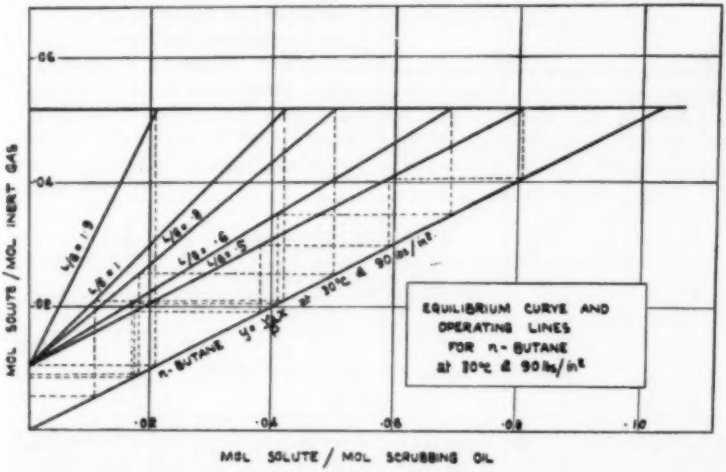


FIG. 4.

The equilibrium curve for butane was obtained from a combination of Raoult's and Dalton's laws. Thus

$$\text{Partial pressure} = V_p \,.\, X = P_y,$$

where V_p = vapour pressure of liquid butane at working temperature.
X = mols. of butane in solution per mols. of scrubbing oil.
P = Total working pressure.

y = mols. of butane vapour in equilibrium with X under working conditions.

A typical graph is given in Fig. 4 for illustration—namely, that for working under 6 atms. and at 30° C. The number of ideal plates necessary in the column to strip off 80 per cent. of butane with different values of liquid to gas ratios all pass through the point

$$X = 0; \quad y = 0{\cdot}0104,$$

but each has a tangent equal to the L/G (mols. liquid/mols. gas) ratio. Thus five operating lines were drawn the tangents of which are

$$1{\cdot}9; \quad 1; \quad 0{\cdot}8; \quad 0{\cdot}6; \quad 0{\cdot}5.$$

The number of ideal plates in the column was found by counting the steps taken to drop from 0·052 mol. per cent. of butane content of the gas to 0·0104 mol. In Fig. 5 is shown a plot of L/G ratio against number of ideal

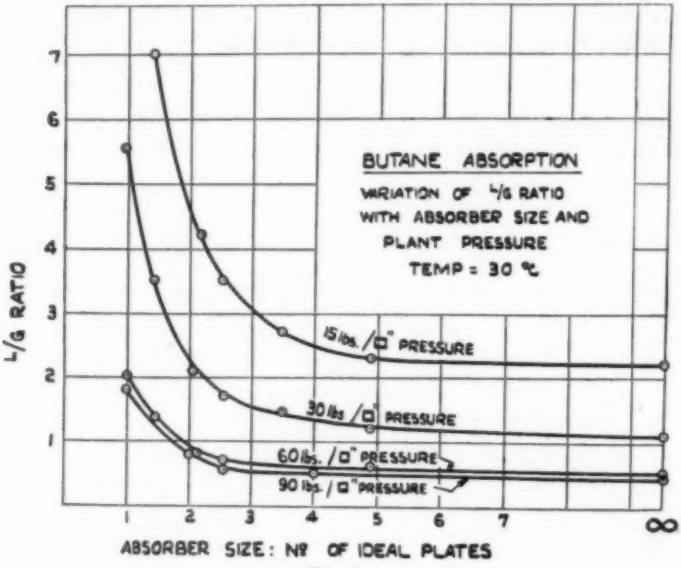


Fig. 5.

plates necessary in the absorber for absorbers working under 15 lbs./sq. in., 30 lbs./sq. in., 60 lbs./sq. in., and 90 lbs./sq. in. We note that there is a point at the bend of each curve which gives the most economical combination for working under any one set of pressure and temperature. Table III gives such points and exit oil percentage saturation for the different working pressures.

These ideal plates would be sufficient for the purpose if they were procurable. But actually the vapour above the liquid in the tray is never in equilibrium with the liquid. Hence for each ideal plate calculated as necessary we need actually more than one bubble tray. When, say, four

TABLE III.

Pressure, lbs./sq. in.	Liquid/Gas Ratio.	Absorber Height in Number of Ideal Plates.	Exit Oil, Percentage Saturation.
15	2·3	5	87
30	1·4	4·5	84
60	0·6	3·5	75
90	0·55	3·0	69

plates are required in practice, while theory demands only one ideal plate to achieve certain results, each actual plate is supposed to be doing only one-quarter of its theoretical performance, and it is considered as being of 25 per cent. efficiency. Of course in actuality the load of one ideal plate may or may not be equally shared by the four; but this supposition of each being 25 per cent. efficient leads to the results in an easier manner. Again, the efficiency of a bubble plate depends on L/G ratio, working temperatures and pressures, gas velocity in absorber shell, nature of gas aside from the characteristics imparted by the design of the plate and the caps themselves. But the total cost of the absorber, as will be seen later, is about 4 to 5 per cent. of the total cost of the plant. Hence any variation in the efficiency of the trays will be of the second order of small quantities in estimating the relative costs for the different plants. These considerations caused the author to take 25 per cent. efficiency in relation to butane absorption by the bubble plates throughout the design.

To calculate the actual height of the column, a distance of 2 ft. between centre lines of successive plates is allowed, while 3 ft. above the topmost plate and 3 ft. below the first were considered adequate. The level of oil above the bottom of the column is 1 ft. Coolers could be placed here to abstract the heat of absorption so that incoming gas remains at 30° C. Thus we get Table IV.

TABLE IV.

Pressure, lbs./sq. in.	Theoretical Height in Ideal Plates.	Actual Number of Plates.	Actual Height in Feet.
15	5	20	46
30	4·5	18	42
60	3·5	14	34
90	3·0	12	30

The diameter of the columns must be such that, with the given height between plates and existing working conditions, entrainment is not excessive. "Entrainment signifies the upward displacement of liquid particles from plate to plate caused by dynamic action of the vapour," is how Souders and Brown put it. The effects of entrainment are:

(1) Loss of liquid overhead.
(2) Increase in quantity of liquids flowing from plate to plate due to abrupt changes in vapour load.
(3) Decrease of plate efficiency.

Many factors affect entrainment which are not yet definitely known, but assuming that the mass velocity of gas upwards through the free space of the column controls the quantity of entrainment in the same way as the upward mass velocity of any fluid is able to suspend solid or liquid particles, depending on their density and size, Souders and Brown arrived at

$$W = C\{d_2(d_1 - d_2)\}^{\frac{1}{2}}$$

where W = mass velocity of the gas allowable in lbs./sq. ft./hr.
C = a constant depending on distance between plates.
d_1 = density of liquid in lbs./cu. ft.
d_2 = density of gas in lbs./cu. ft.

From charts which these authors give, C for a distance of 24 in. between plates is 640, and they advise the employment of a safety factor. Actual practice showed C to be 400, 400 and 440 for this condition, so 400 was chosen. They also give a chart for W, the maximum allowable mass velocity in lbs./sq. ft./hr. for values of $d_2(d_1 - d_2)$ and C, which should be very useful to the designer.

The densities of methane, ethane, propane and butane are given in the literature, and are put in the second column of Table V. The density of "pentane plus" was calculated from the fact that it had an average mol. wt. of 100.

TABLE V.

Gas.	Density in kg./m.³ at 1 atm. and 0° C.	Per cent. by Vol. of Total Gas.	Weight of Component Gas in kg./m.³
CH_4	0·7168	50	0·3585
C_2H_6	1·3562	30·7	0·4068
C_3H_8	2·02	13·5	0·2727
C_4H_{10}	2·6726	4·2	0·1120
C_5H_{12} +	4·42	1·6	0·0770

Thus density of gas entering the plant at N.T.P. is 1·2270 kg./m.³ or 0·077 lb./cu. ft. As the gas travels upwards it gets lighter, hence the diameter should be slightly bigger. But, owing to the relatively small proportion of abstracted gases and allowing for the 3 ft. dome on top instead of the 2ft. distance, it was considered sufficient to design according to the entering

TABLE VI.

	15 lbs./sq. in. 30° C.	30 lbs./sq. in. 30° C.	60 lbs./sq. in. 30° C.	90 lbs./sq. in. 30° C.
Gas density, lbs./cu. ft.	0·0695	0·139	0·278	0·417
Oil density, lbs./cu. ft.	52·9	52·9	52·9	52·9
$d_2(d_1 - d_2)$	3·67	7·35	14·6	21·9
W, lbs./hr./sq. ft.	750	1,100	1,500	1,900
Gas mass rate, lbs./hr.	14,438	14,438	14,438	14,438
Minimum cross-sectional area of column, sq. ft.	19·3	13·3	9·7	7·6
Diameter of column, ft. and in.	5 00	4 3	3 9	3 3

gas characteristics. The factor of safety taken is sufficient in any case. Thus we get Table VI.

In this way we get our general specifications for absorber columns in the compression absorption plants as tabulated in Table VII.

TABLE VII.

Working Conditions, lbs./sq. in.	Diameter, ft. and ins.	Number of Plates.	Height, ft.
15	5 00	20	46
30	4 03	18	42
60	3 09	14	34
90	3 03	12	30

Now let us turn our attention to the working fluids. We found in Table III the necessary L/G ratios. These are ratios of mols. of liquid (oil) to mols. of inerts flowing through the absorber countercurrently to each other. As 1 mol. of gas at N.T.P. (neglecting deviations) occupies 22·4 m.^{3}, it will occupy 879 cu. ft. at 30° C. and normal pressure. Also only 80·7 per cent. of the 5,000,000 cu. ft. which constitute the daily flow are inerts, therefore our rate of "inerts" flow to the plant is 193 kg.-mols./hr. This, multiplied by the L/G ratio, gives us the rate of oil flow in kg.-mol./hr.

Remembering that the mol. wt. of our oil is 200, we get the rate of flow in tons of oil/hr. (see Table VIII).

TABLE VIII.

	15 lbs./sq. in.	30 lbs./sq. in.	60 lbs./sq. in.	90 lbs./sq. in.
L/G ratio . . .	2·3	1·4	0·6	0·55
Kg.-mol. oil/hr. . .	444	270	116	106
Tons oil/hr. . . .	88·8	54·0	23·2	21·2

Finally we must compute the composition of our exit gas and solute in rich oil. Plate efficiency depends on the nature of the gas employed. Thus a 25 per cent. efficient plate for butane is not necessarily 25 per cent. efficient for propane. The efficiency seems to increase with increase in mol. wt., but not lineally. We will assume that it is only half the value for absorbing propane as for the absorption of butane and "pentane plus." The L/G ratio operating is, of course, the same as for butane, since it is based on the inerts mols. flowing. Hence equilibrium curves for each component were plotted, and operating lines were drawn in such a way that their tangent was equal to the L/G operating, and steps equal numerically to the number of ideal plates in the column just fixed the lines at their extremities. The component gas mol. ratios to mols. inerts and to mols. oil were read from the graph (Fig. 6). Since average mol. wt. for "pentane plus" was 100, it was treated as if it were heptane. Even if it were equivalent to hexane, this is not important, since it is practically all absorbed. Table IX shows the results.

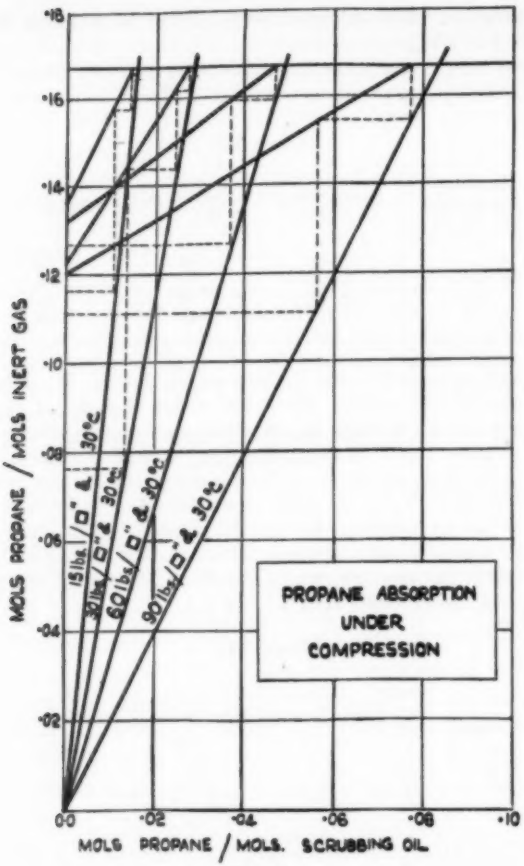


FIG. 6.

TABLE IX.

	15 lbs./sq. in.	30 lbs./sq. in.	60 lbs./sq. in.	90 lbs./sq. in.
Number of actual plates	20	18	14	12
Number of ideal plates for—				
(*a*) C_5H_{12} +	5	4·5	3·5	3·0
(*b*) nC_4H_{10}	5	4·5	3·5	3·0
(*c*) C_3H_8	2·5	2·25	1·75	1·5
L/*G* ratio	2·3	1·4	0·6	0·55
Mols. C_3H_8/mol. inerts in exit gas	0·137	0·123	0·132	0·121
Mols. C_5H_{12} + /mol. inerts in exit gas.	0·0	0·0	0·0	0·0
Composition of solute in exit oil—				
1. Mols. solute/mols. oil	0·041	0·071	0·155	0·190
2. (*a*) C_5H_{12} +	0·009	0·014	0·033	0·036
(*b*) nC_4H_{10}	0·018	0·030	0·069	0·076
(*c*) C_3H_8	0·014	0·027	0·053	0·078

2. *Refrigeration.* The same considerations were taken here, and the design follows exactly similar steps. Thus we will have the final results in form of Table X. (See Figs. 7 and 8.)

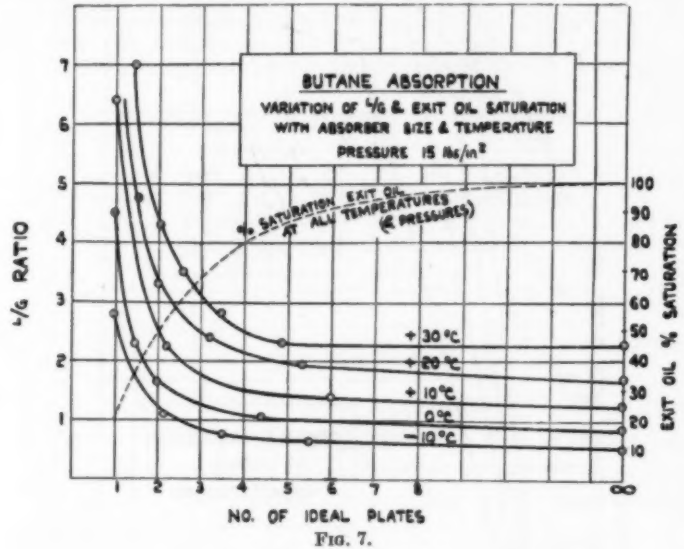


FIG. 7.

TABLE X.

	−10° C. and 1 atm.	0° C. and 1 atm.	10° C. and 1 atm.	20° C. and 1 atm.	30° C. and 1 atm.
Gas density, lbs./cu. ft. .	0·080	0·077	0·074	0·072	0·0695
Oil density, lbs./cu. ft. .	55·0	54·2	53·6	53·1	52·9
$d_2(d_1 - d_2)$ . . .	4·31	4·16	3·96	3·82	3·67
W, lbs./hr./ft.² . .	950	900	900	800	750
Gas mass rate, lbs./hr. .	14,438	14,438	14,438	14,438	14,438
Diameter of tower, ft. and ins. . . .	4 6	4 6	4 6	4 9	5 00
Height of tower, ft. .	34	40	42	46	46
Number of actual plates.	14	17	18	20	20
Number of ideal plates for—					
(*a*) C_3H_{12} . . .	3·5	4·2	4·5	5	5
(*b*) nC_4H_{10} . . .	3·5	4·2	4·5	5	5
(*c*) C_3H_8	1·75	2·1	2·25	2·5	2·5
L/G ratio	0·75	1·1	1·45	1·95	2·3
Tons oil/hr.	29	42·4	56	75·2	88·8
Mol. propane/mol. inerts in exit gas . .	0·134	0·131	0·132	0·131	0·137
Mol. C_3H_{12} + /mol. inerts in exit gas . .	0·0	0·0	0·0	0·0	0·0
Composition of solute—					
1. Mol. solute/mol. oil	0·127	0·089	0·068	0·049	0·041
2. (*a*) C_3H_{12} + . .	0·026	0·018	0·014	0·010	0·009
(*b*) nC_4H_{10} . .	0·056	0·038	0·029	0·021	0·018
(*c*) C_3H_8 . .	0·045	0·033	0·025	0·018	0·014

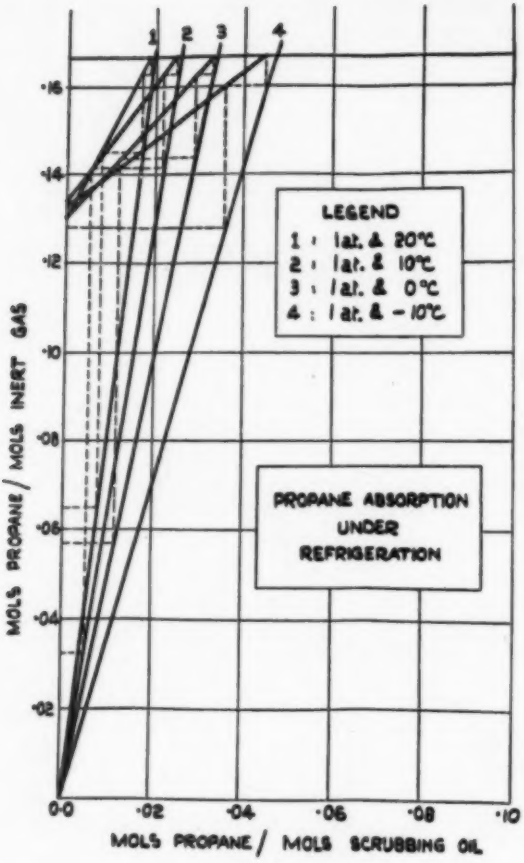


FIG. 8.

CONCLUSIONS ON ABSORBER DESIGN.

1. Increase of working pressure decreases smallest practicable L/G ratio required for our conditions (hence reduced amount of oil circulating). However, a limiting value for the pressure is found above which any further increase in pressure does not affect the smallest practicable L/G ratio. (Fig. 9.)

2. Increase of working pressure decreases height of absorber required for a given L/G ratio. (Fig. 10.)

3. Decrease in working temperature decreases lineally the least practicable L/G ratio required for our given conditions. (Fig. 11.)

4. Decrease of working temperature decreases the absorber height required for a given L/G ratio. (Fig. 10.)

5. For a given L/G ratio the best absorber height (in number of ideal plates) is the same whether we arrive at the value of the given L/G ratio by manipulating our pressure or temperature. Thus the curves in Fig. 12 are coincident. We also see that between 1 and 4 atms. and $-10°$ C. and $+30°$ C., 1° C. decrease in temperature has approximately the same effect

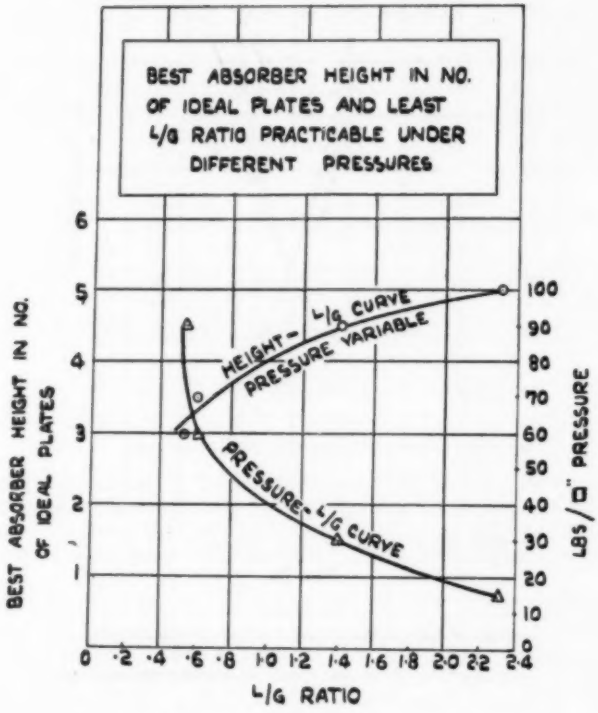

BEST ABSORBER HEIGHT IN NO. OF IDEAL PLATES AND LEAST L/G RATIO PRACTICABLE UNDER DIFFERENT PRESSURES
BEST ABSORBER HEIGHT IN NO. OF IDEAL PLATES
HEIGHT - L/G CURVE PRESSURE VARIABLE
PRESSURE - L/G CURVE
LBS/□" PRESSURE
L/G RATIO
0 ·2 ·4 ·6 ·8 1·0 1·2 1·4 1·6 1·8 2·0 2·2 2·4
1 2 3 4 5 6
10 20 30 40 50 60 70 80 90 100

FIG. 9.

as 1·12 lbs./sq. in. increase in pressure. Hence a column working at 4 atms. and 30° C. will be of the same height and require the same L/G ratio as one working at 3 atms. and 16·6° C. or 2 atms. and + 3° C., etc. This principle affords us a ready means of finding absorber height and L/G ratio for any system of pressure and temperature between the two limits given above.

6. Percentage saturation of exit oil increases with absorber height, and is constant for a given size of absorber, being independent of both temperature and pressure. This is evident, for although more gas will dissolve in the oil under higher pressures and lower temperatures, solubility of the gas is also increased, leaving percentage saturation a constant. (Fig. 7.)

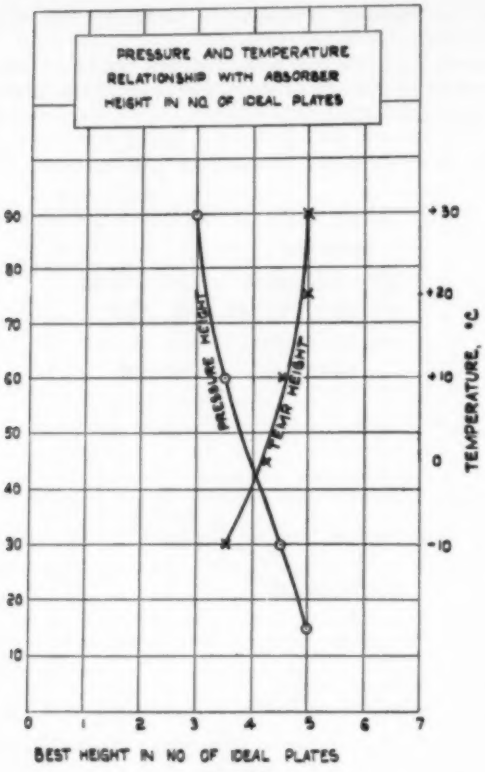

PRESSURE AND TEMPERATURE
RELATIONSHIP WITH ABSORBER
HEIGHT IN NO. OF IDEAL PLATES
PRESSURE HEIGHT
TEMP. HEIGHT
TEMPERATURE, °C
+30
+20
+10
0
-10
90
80
70
60
50
40
30
20
10
0 1 2 3 4 5 6 7
BEST HEIGHT IN NO OF IDEAL PLATES

FIG. 10.

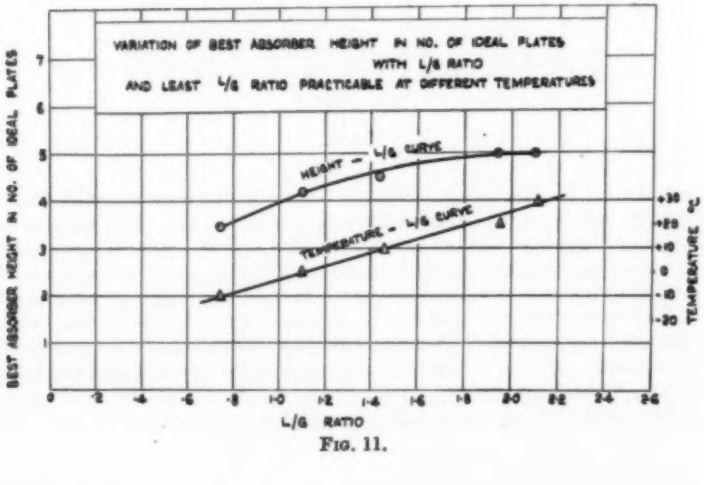

VARIATION OF BEST ABSORBER HEIGHT IN NO. OF IDEAL PLATES
WITH L/G RATIO
AND LEAST L/G RATIO PRACTICABLE AT DIFFERENT TEMPERATURES
HEIGHT — L/G CURVE
TEMPERATURE — L/G CURVE
BEST ABSORBER HEIGHT IN NO. OF IDEAL PLATES
TEMPERATURE °C
+30
+20
+10
0
-10
-20
0 ·2 ·4 ·6 ·8 1·0 1·2 1·4 1·6 1·8 2·0 2·2 2·4 2·6
L/G RATIO

FIG. 11.

These conclusions apply specifically in our chosen problem. But it is the author's contention that they also apply generally, with modifications to actual values of the limits. In fact, one of the aims of this paper is to indicate the general behaviour of the different components of an oil-absorption plant by studying this particular set of working conditions.

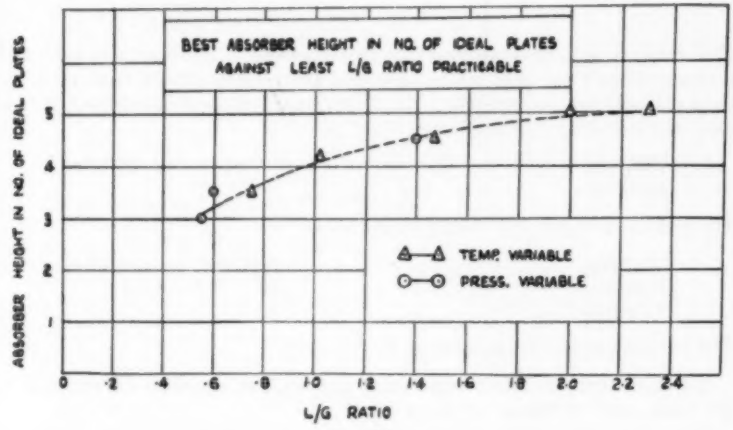


FIG. 12.

THE STABILIZER.

From Tables IX and X the composition of feed to the stabilizer in terms of percentages of each component to total gas in solution can be calculated. For ease of reference the cases for compression system were put in the same table as for the refrigeration absorption. These are shown in Table XI.

TABLE XI.

	15 lbs./ sq. in. 30° C.	30 lbs./ sq. in. 30° C.	60 lbs./ sq. in. 30° C.	90 lbs./ sq. in. 30° C.	15 lbs./ sq. in. −10° C.	15 lbs./ sq. in. 0° C.	15 lbs./ sq. in. 10° C.	15 lbs./ sq. in. 20° C.
C_3H_8 .	34·4	38·0	34·2	42·8	35·6	37·1	36·8	36·7
C_4H_{10} .	44·3	42·3	44·6	38·7	43·9	42·6	42·7	42·8
C_5H_{12}+	21·3	19·7	21·2	18·5	20·5	20·3	20·5	20·5

It will be seen that in all cases the approximate proportion

$$C_3 : C_4 : C_5 = 40 : 40 : 20$$

holds with an error of maximum value of 10 per cent. Hence it is considered that one design of a stabilizer—made to handle the worst case—will be sufficient; the only effect is to increase the factor of safety by few per cent. in the more favourable cases. The effect on the costing estimate is considered to be negligible. Therefore a stabilizer to handle the maximum proportion of propane is designed on the lines indicated by Robinson

in his *Elements of Fractional Distillation*. This condition is at 90 lbs./in.^{2} and 30° C., where the feed is—

C_3H_8	42·8	per cent. of total
C_4H_{10}	38·7	,, ,,
C_5H_{12} +	18·5	,, ,,
	100·0	,, ,,

This mixture is to be separated into two fractions. The distillate will have no more than 1 per cent. of butane, and the residue should have no more than 0·1 per cent. of propane. If all the distillate were condensed, it will have the following composition:

Propane	99	per cent. of total
Butane	1	,, ,,

The residue, assuming no losses, would be—

Propane	0·1	per cent. of total
Butane	67·4	,, ,,
"Pentane plus"	32·5	,, ,,

The partial condenser operates at 20° C.

We find that at this temperature the vapour pressure of propane is 8·8 atms., and of butane 2·0 atms.

The condenser being only a partial one, the vapours leaving will be in equilibrium with the condensate. The vapours, of course, have the composition shown above as distillates. The condensate will be the reflux.

From Dalton and Raoult's Laws we form the three equations—

$$8{\cdot}8\,X_p = 0{\cdot}99\,\pi$$
$$2{\cdot}7\,X_B = 0{\cdot}01\,\pi$$
$$X_p + X_B = 1$$

where π = total pressure in condenser.
X_p = mol. fraction of propane in liquid condensate.
XB = mol. fraction of butane in liquid condensate.

Thus the total pressure in the condenser, and hence in the column, is 8·6 atms.

$$X_p = 0{\cdot}960;\ X_B = 0{\cdot}043.$$

Taking a reflux ratio of 3—smaller values having proved inadequate by preliminary calculations on the following lines—for every 100 mols. of gaseous distillate, there will be 300 mols. of condensate. So total C_3H_8 is 387 mols. and total C_4H_{10} is 13 mols., making 400 mols. of vapour coming out of the top of the column. Expressed in percentages, $C_3H_8 = 96{\cdot}75$ per cent., and $C_4H_{10} = 3{\cdot}25$ per cent. All these values are shown on Fig. 13.

Now, with the notations

P_p = partial pressure of propane.
P_B = ,, ,, ,, butane.
P_3 = vapour ,, ,, propane.
P_4 = ,, ,, ,, butane.

the three equations—

$$X_p P_3 = 0{\cdot}9675 \times 8{\cdot}6$$
$$X_B P_4 = 0{\cdot}0325 \times 8{\cdot}6 \text{ and}$$
$$X_p + X_B = 1$$

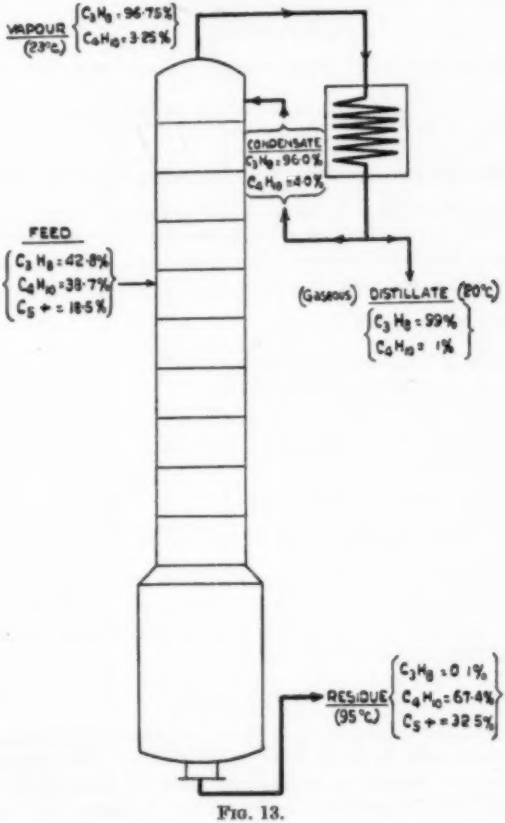


FIG. 13.

are correct and give when solved, by successive approximations, 23° C., the temperature at which these relations hold. Also $P_3 = 9{\cdot}6$ atms., $P_4 = 2{\cdot}1$ atms.; $X_p = 0{\cdot}868$ and $X_B = 0{\cdot}103$. These values are at the topmost plate in the column.

Similarly for the bottom plate

$$P_p = Y_p \times 8{\cdot}6 = 0{\cdot}001\ P_3$$
$$P_B = Y_B \times 8{\cdot}6 = 0{\cdot}674\ P_4$$
$$P_H = Y_H \times 8{\cdot}6 = 0{\cdot}325\ P_7$$

where the suffixes H and 7 are for the heptane fraction or "pentane plus," and Y is the mol. fraction of the component in the vapour phase. By

successive approximation the kettle temperature was found to be 95° C. and $P_3 = 30{\cdot}6$ atms.; $P_4 = 12{\cdot}0$ atms. and $P_7 = 1{\cdot}0$ atm. (very approximately). The mol. fractions in the vapour phase were found to be—

$$Y_P = 0{\cdot}0036$$
$$Y_B = 0{\cdot}953$$
$$Y_H = 0{\cdot}038.$$

To determine the number of plates necessary Sorel's equation was applied—

$$Y_m = \frac{R_m + 1}{V_m} X_{m+1} - \frac{(R_f - 1)X_w}{V_m}$$

where (for the first plate from bottom, numerical values are given)—

Y_m = mol. fraction of propane in m^{th} plate (= 0·004).
V_m = mols. of vapour passing from m^{th} to $m + 1^{\text{th}}$ plate (= 1 + 3 = 4)
X_w = mol. fraction of propane in residue ($R_f - 1$), (= 0·001).
R_f = mols. of feed/mol. distillate.

(R_f is found in the following way :

Let a = mols. of feed/mol. distillate.
b = mols. of residue/mol. distillate.

$$\therefore \quad a - b = 1$$
$$42{\cdot}8a - 0{\cdot}1b = 99$$

Hence
$$a = R_f = 2{\cdot}3$$
$$b = \quad 1{\cdot}3)$$

R_{m+1} = mols. of overflow from $m + 1^{\text{th}}$ to m^{th} plate, ($R_f + 1 = 3{\cdot}3$)

Hence for Plate I $X_1 = 0{\cdot}005$.

This is in equilibrium with a vapour containing Y_1 mols. of propane/mols. of total vapours, which value of Y is read from the curve in Fig. 14. This curve was constructed from the relation

$$8{\cdot}6\ Y_p = X_p P_3$$

and as we know the values of P_3 at three points—kettle, feed and topmost plate—the curve was plotted after substitution. The temperature prevailing at the first plate counting upward from the kettle is 75° C. In this way Table XII was constructed. The plates, of course, are " ideal plates."

TABLE XII.

No. of Plate.	Mol. Fraction of C_3H_8 in Liquid.	Mol. Fraction of C_3H_8 in Vapour.	Temperature, ° C.
I	0·005	0·015	75
II	0·019	0·030	35
III	0·031	0·050	34
IV	0·063	0·100	33·5
V	0·127	0·195	33
VI	0·254	0·375	32·5
VII	0·484	0·64	29

Hence the feed is between sixth and seventh plate from bottom, counting first plate as the one just above the kettle.

Similarly for the rectifying part of the column, counting the topmost plate as the first, we have $X_1 = 0{\cdot}868$, $Y_1 = 0{\cdot}9675$, temperature $= 23°$ C. To calculate composition on the second plate the formula

$$Y_n = \frac{R_{n+1}}{V_n} X_{n+1} + \frac{PX_c}{V_n}$$

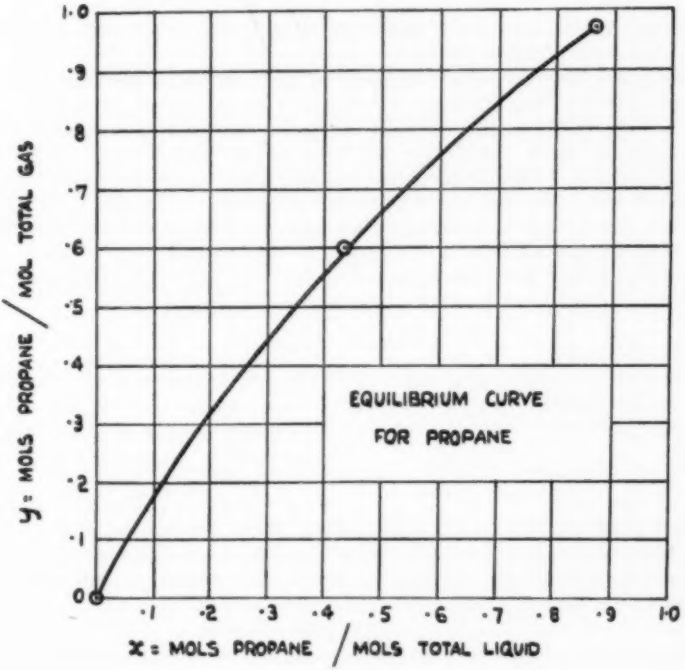


FIG. 14.

was used, where suffix n stands for number of plate above feed counting the topmost as first.

R_{n+1} = mols. of overflow from plate n to $n + 1 = 3$.
$V_n = 4$
P = mols. of distillate withdrawn as product/unit time = 1.
X_c = mols. of propane/mol. distillate.

Substituting we get Table XIII.

Hence the feed is between the fourth and fifth plate counting from top. The fourth plate counting downward becomes the seventh plate from bottom

TABLE XIII.

No. of Plate.	Mol. Fraction of C_3H_8 in Liquid.	Mol. Fraction of C_3H_8 in Vapour.	Temperature, ° C.
I	0·868	0·968	23
II	0·750	0·891	25
III	0·630	0·793	26·5
IV	0·510	0·670	29
V	0·390	0·552	31

upwards. The column would then contain ten plates in all, with the feed above the sixth plate.

Then, assuming an equal efficiency of plate for both sections of the stabilizer, 60 per cent. efficiency can be taken as an average established by practice for fractionating columns. The exhaustive sections will then consist of ten plates, while the rectifying section will be made of seven plates, giving a column of seventeen plates. The feed should enter above the tenth and below the eleventh, counting upward. Allowing 1 ft. 6 in. between centre lines of successive plates and 2 ft. above the topmost, the height of the column—not including kettle—will be 26 ft.

The diameter of the tower is limited again by the amount of entrainment allowable. Using the same principle as for the absorber,

$$W = C\{d_2(d_1 - d_2)\}^{\frac{1}{2}}$$

we work on the values of d_2 and d_1 that will give us the smallest value for W, *i.e.* the largest necessary diameter. This means d_1 must be at its lowest, which state of affairs exists on the top plate of the column. Here

$$X_p = 0{\cdot}868 \qquad Y_p = 0{\cdot}891$$
$$X_B = 0{\cdot}132 \qquad Y_B = 0{\cdot}109$$

while X_H and Y_H do not exist appreciably. From the data supplied by the Propane and Butane Handbook d_1, the density of the liquid on the plate comes out to be 32 lbs./cu. ft. To find d_2, the density of the vapours, Table XIV is shown.

TABLE XIV.

	Density in kg./m.³ N.T.P.	Per cent. by Vol. of Total.	Weight of Component in kg./m.³
C_3H_8	2·02	0·891	1·8
C_4H_{10}	2·67	0·109	0·29

Hence density at N.T.P. is 0·131 lb./cu. ft., while at 8·6 atms. and 23° C. it is 1·04 lbs./cu. ft. Thus, taking a value of 400 for C, we get the maximum allowable mass rate for the vapours 1800 lbs./hr./ft.² Working with the oil obtained from the absorber at 90 lbs./in.² and 30° C., we have to stabilize 106 kg.-mols. of oil/hr. containing 0·196 mol. of solute/mol. oil, giving a rate of 20·8 kg.-mols. of gas/hr. For every 2·3 mols. of feed, 1 mol. distils over, while 3 mols. reflux back. This reflux has naturally been vapour

before condensation. Therefore the vapours passing up the column are 36·2 kg.-mols./hr., and at N.T.P. would occupy 22·4 m.^{3} per mol. Changing over into British units and multiplying by the density of the gas, we have the mass rate of 471 lbs./hr. of vapours passing upwards. Hence the minimum cross-sectional area of the free space should be 0·26 sq. ft. or, say, a diameter of 0·18 ft. This is for the rectifying section of the column. In the stripping section a mass of oil is flowing downward, and using the formula—

$$a = \frac{Q}{4{\cdot}4}h$$

where a = area of down-comer in sq. in.
Q = quantity of oil in U.S. gallons per minute.
h = liquid head equal to the height of the overflow weir of 3 in.

the diameter of the down-comer was found to be 4 in. To give a final factor of safety and make the column capable of handling an overload, it was decided to make it of 1 ft. 6 in. diameter throughout its length, excepting, of course, the kettle. Thus a summary of the chief specifications of the stabilizer is :—

Working pressure	8·6 atms.
Top temperature	23° C.
Kettle temperature	95° C.
No. of plates	17
(*a*) Exhausting	10
(*b*) Rectifying	7
Height of column	26 ft.
Distance between plates	1 ft. 6 in.
Dome height	2 ft.
"h" over weir	3 in.
Diameter of column	1 ft. 6 in.

The Kettle.—In designing the kettle we need to know the quantity of heat required per unit time to fulfil the requirements set by the stabilizer design. The heat balance for the compression absorption process working at 6 atms. and 30° C. is given in Table XV.

The second part of the table is essential for the partial condenser design later on. We see that 762,000 B.Th.U. have to be absorbed by the condenser per hour.

The type of kettle adopted is the standard vertical tube evaporator with a circular down-comer in the centre. It is shown schematically in Fig. 15. The tubes are 2 in. in diameter, to facilitate cleaning and scaling. They would be arranged concentrically, so that each is in an approximate square of 3 in. side. The formula adopted is one using overall values, *i.e.*

$$q = UA\Delta T$$

where q = rate of heat transfer in B.Th.U./hr.
A = heating surface in sq. ft.
ΔT = mean temperature difference between steam and boiling liquid.
U = overall coefficient in B.Th.U./hr./ft.^{2}/°F. of ΔT.

TABLE XV.

Material.	Quantity, lbs./hr.	Temperature, ° F.	Heat Content, B.Th.U./lbs. from 30° C.	Total Heat Required above 30° C., B.Th.U./hr.
Input.				
Oil	47,500	203	58·5	2,780,000
Propane (vapour) . .	860	203	214·0	184,000
Reflux (23° C.) . .	2,580	203	220·0	568,000
Butane (vapour) . .	510	203	214·0	2,140
Butane (liquid) . .	1,000	203	70·0	70,000
"Pentane plus" . .	840	203	60·0	50,500
Losses (2·5%) . . .	—	—	—	75,000
Total . . .	—	—	—	3,729,640
Output.				
Oil	47,500	203	58·5	2,780,000
Propane (liquid dist.) .	860	73	−8·0	−6,880
Butane (liquid dist.) .	10	73	−8·0	− 80
Butane (residue) . .	1,000	203	70·0	70,000
"Pentane plus" . .	840	203	60·0	50,000
Losses	—	—	—	75,000
Total . . .	—	—	—	2,968,140

ΔT is taken as the "apparent temperature drop," *i.e.* the arithmetical difference between the temperature of steam (150 lbs. steam) and oil at 203° F. This saturated steam at 150 lbs./sq. in. is at 358·43° F. Hence $\Delta T = 155°$ F.

No value is given in the literature for U for all kinds of evaporators. All agree that data to enable one to use a general formula for evaluating this coefficient is deplorably lacking. It seems the best way would be to build a small-scale evaporator of the type chosen and arrive at a suitable value for U. But the little data which are given by different authors indicate that a value of 100 could well be assigned for U for a copper evaporator of the type we are using. Thus, as we have to transmit 3,800,000 B.Th.U. per hour, an area of 250 sq. ft. would be sufficient. Using a 3 ft. length of 2-in tubes, each has 1·5 sq. ft. heating surface. Hence we need 167 such tubes. Assuming, for approximate design, a square of 3 in. for each, and allowing a down-comer of 9 in. diameter, we decide on a kettle having 4 ft. overall diameter (allowance for drains, etc., was made). Two feet are allowed free space above the kettle to reduce entrainment to a low value. The level of the oil, incidentally, as measured from the lowest point of the tubes, has an optimum value for giving the highest value for U. This level, several authors agree, seems to be between 10 and 20 in. for tubes of the order of 2·5 to 3·5 ft. long. The value of 15 in. is advocated. A level indicator was incorporated in the design to facilitate observing the level. But, of course, this level should be set automatically by the exit oil pipe being bent to have its delivery end at that level.

The amount of steam required, assuming heat absorbed is due to condensation to 100° C. water temperature, is 3750 lbs./hr.

Kettles for Different Operating Conditions.—Although it was said that the same column would operate satisfactorily for the other conditions—in fact,

slightly better—the kettles would be very different for each case. This is because the L/G ratio varies between 2·3 and 0·55—*i.e.* the amount of oil to be heated has greater variation with the different cases.

Naturally the first step to compute the quantity of heat per hour is neces-

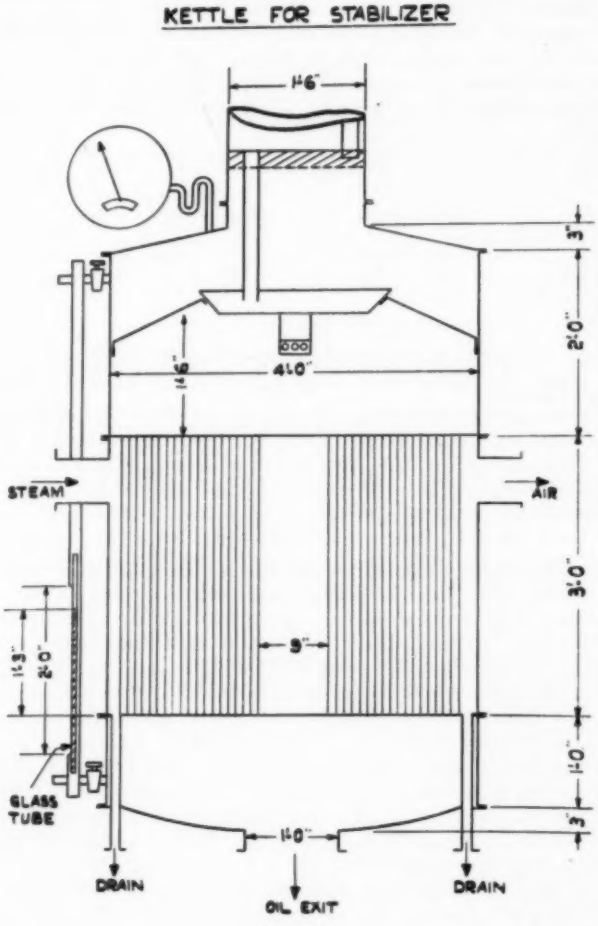


FIG. 15.

sary in each case. It was seen that this quantity was largely dependent on the amount of oil and propane circulated (butane and "pentane plus" accounting for less than $\frac{1}{2}$ per cent. of total heat required). Besides, the amount of heat required to heat the butane and "pentane plus" is constant, since there is a constant rate of these materials flowing between a constant

temperature difference of 65° C. Hence their heat requirement is 122,600 B.Th.U./hr. throughout. This assumes that the feed temperature is always 30° C. For the refrigeration absorption a heat exchanger is fitted to bring the oil up to 30° C. On these bases Table XVI was constructed. The heating surface was calculated for each kettle by the general formula $q = UA\Delta T$.

ΔT is constant for all kettles, and U was also taken to be 100 throughout, for the reasons outlined above. Hence $q \propto A$. So A was found for each kettle by simple proportion. Similarly, the quantity of steam is proportional to q, working under similar operating conditions throughout.

TABLE XVI.

	1 atm. 30° C.	2 atms. 30° C.	4 atms. 30° C.	6 atms. 30° C.	1 atm. −10° C.	1 atm. 0° C.	1 atm. 10° C.	1 atm. 20° C.
Lbs. oil/hr.	197,000	121,000	54,000	47,500	65,000	95,000	125,000	168,000
Lb. C_3H_8 dist./hr.	600	780	615	860	628	675	675	675
Lbs. reflux/hr.	1,800	2,340	1,845	2,580	1,884	2,025	2,025	2,025
Heat required in B.Th.U./hr. for—								
(*a*) Oil	11·5 × 10^6	7·1 × 10^6	3·16 × 10^6	2·78 × 10^6	3·8 × 10^6	5·5 × 10^6	7·3 × 10^6	9·7 × 10^6
(*b*) Propane	128,000	167,000	131,500	184,000	134,000	144,000	144,000	144,000
(*c*) Reflux	396,000	515,000	406,000	568,000	415,000	446,000	446,000	446,000
(*d*) $C_4H_{10} + C_5H_{12}$+	122,600	122,600	122,600	122,600	122,600	122,600	122,600	122,600
(*e*) Losses (approx. 2·5%)	300,000	175,000	75,000	75,000	100,000	150,000	175,000	250,000
Total B.Th.U./hr. required.	12·5 × 10^6	8·1 × 10^6	3·9 × 10^6	3·7 × 10^6	4·6 × 10^6	6·4 × 10^6	8·2 × 10^6	10·7 × 10^6
Heating surface, sq. ft.	830	535	260	250	310	430	540	725
Lbs. steam/hr.	12,400	8,000	3,750	3,750	4,500	6,300	8,150	10,600

The Condenser for the stabilizer would be a horizontal tubular type. The propane–butane vapours to be partly condensed would flow on the outside of the pipes, while cooling water (at 45° F.) would flow countercurrently inside the tubes. (If water is not available at this temperature, the compressed propane vapours could be used to cool it down.) The total amount of heat to be absorbed was found, from Table XV, to be for compression system of 6 atms., 762,000 B.Th.U./hr. Again, taking the arithmetical temperature difference for a first approximation—instead of the more exact logarithmic mean—it is equal to 28° F. The *Chemical Engineer's Handbook* gives values for U in this type of heat transmission from 60 to 150 B.Th.U./hr./sq. ft./1° F.ΔT. For safety 60 was adopted, and the cooling surface was found to be 475 sq. ft. It was decided to have two condensers, each providing 250 sq. ft. of cooling area. The upper one is inclined so that the condensate flows by gravity to the second and lower one. The lower condenser has an equal inclination, but in the opposite direction. The cooling water is pumped to flow upwards from the lower end of the second condenser.

Using 6 ft. tubes of 1·5 in. diameter, the cooling surface provided by each pipe amounts to 1·25 sq. ft. Hence we need 200 such tubes for each condenser, which makes the diameter of each condenser of the order of 2·1 ft.—say, 2 ft. 6 in. The length is 7 ft.—allowing 6 in. on each side of the bank of tubes.

Forty thousand lbs. of water have to be circulated each hour—*i.e.* 4000 gals./hr.

This more or less detailed design is for the specific condition of working under an absorber pressure of 6 atms. For the other cases Table XVII shows the chief characteristics. The heat to be abstracted is, of course, that for condensing the propane vapours into distillate and refluxing (very approximately).

TABLE XVII.

	1 atm. 30° C.	2 atms. 30° C.	4 atms. 30° C.	6 atms. 30° C.	1 atm. −10° C.	1 atm. 0° C.	1 atm. 10° C.	1 atm. 20° C.
B.Th.U./hr. abstracted .	424,000	682,000	537,500	752,000	549,000	590,000	590,000	590,000
Cooling surface, sq. ft. .	255	405	320	475	330	370	370	370
Number of condensers .	1	2	1	2	1	2	2	2
Sq. ft. cooling per condenser . .	275	210	350	250	350	200	200	200
Number of tubes/cond. .	220	168	280	200	280	160	160	160
Diameter, ft. and in. .	2 9	2 3	3 6	2 6	3 6	2 00	2 00	2 00
Gallons water/hr. . .	2,200	2,500	2,700	4,000	2,800	3,000	3,000	3,000

THE STRIPPER.

To conserve space, the stripper design for both refrigeration and compression systems will be dealt with simultaneously. The stripper is a column working on the same principles as the absorber, but in the opposite direction. Gasoline will be desorbed by the steam—the "inert" gas—from the oil. The steam comes directly from a reducing valve, which throttles it down from its high pressure at the exit of the preheater to a pressure just sufficiently above 1 atm. to overcome the friction plus the static head offered by the column. As it is a throttling process, total heat of the steam remains constant (any book on thermodynamics would prove this statement). Its temperature is 359° F. or 182° C. Of course the gasoline content in the steam is zero at the beginning.

The oil entering the absorber was assumed to be gas-free; hence stripping must proceed until the assumption is practically valid, *i.e.* $x_2 = 0$ and $Y_2 = 0$. Working with $C_5H_{12}+$ as a basis for the design, since it interests us most, the design follows exactly the same steps we traced in designing the absorber. (Since the vapour pressure of butane is higher than that of "pentane plus" at equal temperatures, it is obvious that with the existing proportions, by the time the "pentane plus" is stripped all the butane has already flashed over.)

The oil leaving the stabilizer would be heated to the temperature of the incoming steam—*i.e.* 182° C.—through heat exchangers and a preheater. The pressure in the stripper will be adjusted through the condenser, and reducing valve, to be 1 atm. "Pentane plus" being treated like heptane, it has a vapour pressure of 6·7 atms. at the stripper temperature. The equilibrium curve was thus constructed—

$$Y = \frac{V_H}{P}\chi$$

As x_1, from Table IX, is 0·036, and as this has not changed in its passage through the stabilizer, operating lines passing through ($x_2 = 0$,

$y_2 = 0$) and intersecting the vertical through $x_1 = 0{\cdot}036$ at y_1 were drawn. The operating line that gave the maximum L/G ratio (*i.e.* minimum steam required) and a fairly reasonable number of ideal plates was chosen in each case. Theoretically an infinite number of plates are required in each case to strip the oil completely. But actually a finite number is found sufficient to make the amount of gas in the oil negligible. Plate efficiency, height between plates, and all other considerations of this nature were taken here the same as in the absorber. Table XVIII gives the results arrived at.

TABLE XVIII.

	1 atm. 30° C.	2 atms. 30° C.	4 atms. 30° C.	6 atms. 30° C.	1 atm. −10° C.	1 atm. 0° C.	1 atm. 10° C.	1 atm. 20° C.
Number of ideal plates	7	8	8	7	7	6	8	7
L/G ratio	4·5	4·5	4·0	3·3	4·5	4·5	4·5	4·5
y_1 = mols. C_5H_{12}+/mols. steam	0·040	0·062	0·132	0·130	0·120	0·080	0·062	0·040
Kg.-mols. live steam/hr.	98·5	60	29	26·5	32·2	47·1	63·2	83·6
Lbs. steam/hr.	3920	2380	1150	1050	1280	1870	2500	3320
Actual number of plates (total)	28	32	32	28	28	24	32	28
Number of strippers	2	2	2	2	2	2	2	2
Plates in each	14	16	16	14	14	12	16	14
Height of each stripper, ft.	32	36	36	32	32	28	36	32
Diameter of stripper, ft. and in.	3 00	2 3	1 9	1 6	1 6	2 00	2 6	2 9

Two strippers in series were put instead of one to reduce the height.

In deciding the diameter of the columns the same principles with regard to entrainment which were taken in the case of the absorber and stabilizer were followed here. The density of the gases at 1 atm. and 359° F. was calculated as indicated in Table XIX, that of steam being extrapolated from the tables given in the *Chemical Engineer's Handbook*. The density of the oil

TABLE XIX.

	1 atm. 30° C.	2 atms. 30° C.	4 atms. 30° C.	6 atms. 30° C.	1 atm. −10° C.	1 atm. 0° C.	1 atm. 10° C.	1 atm. 20° C.
Mols. C_4H_{10}/mols. exit gas	0·080	0·133	0·276	0·273	0·262	0·169	0·129	0·084
Total mols. solute per mol. exit gas	0·120	0·195	0·408	0·403	0·382	0·249	0·191	0·124
Per cent. steam of total gas	89·4	83·5	71·0	71·2	72·4	80·1	83·9	88·9
Per cent. nC_4H_{10} of total exit gas	7·1	11·1	19·6	19·4	18·8	13·5	10·8	7·5
Per cent. C_5H_{12}+ of total exit gas	3·6	5·2	9·4	9·3	8·7	6·4	5·2	3·6
Weight of steam in exit gas, lbs./cu. ft.	0·0277	0·0258	0·0220	0·0221	0·0224	0·0248	0·0260	0·0278
Weight of C_5H_{12}+ in exit gas, lbs./cu. ft.	0·0056	0·0086	0·0156	0·0154	0·0144	0·0106	0·0086	0·0056
Weight of C_4H_{10} in exit gas, lbs./cu. ft.	0·0071	0·0111	0·0196	0·0194	0·0188	0·0135	0·0108	0·0075
Exit gas density, lbs./cu. ft.	0·0404	0·0555	0·0472	0·0569	0·0556	0·0489	0·0454	0·0409
Oil density, lbs./cu. ft.	45·4	45·4	45·4	45·4	45·4	45·4	45·4	45·4
$d_2(d_1 - d_2)$	1·83	2·53	2·14	2·58	2·53	2·22	2·06	1·85
W_1, lbs./hr./sq. ft.	550	620	600	640	620	610	590	560
Minimum cross-sectional area, sq. ft.	7·12	3·84	1·92	1·64	2·07	3·07	4·24	6·00
Diameter of stripper, ft. and in.	3 00	2 3	1 9	1 6	1 6	2 00	2 6	2 9

at this temperature was arrived at from the formula given in the International Critical Tables—

$$v_t = v_{15.56}[1 + \alpha(t - 15.56°) + \beta(t - 15.56°)]$$

where $\alpha = (2.320 - 1.7S) \times 10^{-3}$

$\beta = (4.86 - 4.5S) \times 10^{-6}$

v_t = volume in cm.^{3} at t ° C.

S = sp. gr. at 15° C.

As it is only an approximation, the accuracy was not considered to be any greater by taking the gas content into account. The rest of the table has the same significance as before.

Accessories.

Accessories to the Stripper.—The oil coming out from the stabilizer has to be heated up to 182° C. before entering the stripper. This is accomplished by two exchangers and a steam preheater. In the first exchanger (No. 1) the stripped oil gives away part of its heat to the entering oil. As much of this heat as it is possible to recover should pass on to the rich oil, since the lean oil is to be cooled. The lower limit to the temperature of the lean oil is 110° C., since the rich oil enters the exchanger at 95° C. As the rate of oil is practically constant and equal in both directions, and the specific heats are also the same, the temperature of the exit rich oil will be 155° C., assuming a loss of 15 per cent. This hot fat oil will be further heated at the expense of the vapours from the stripper in exchanger No. 2. Since the rate of the steam passing through the preheater, the temperature drop in this steam and the final temperature of the rich oil are fixed by other considerations, the temperature of the oil leaving preheater No. 2 will be definitely fixed by these requirements. The steam preheating the oil is the same that later on will strip the gasoline from it. Initially it is at 250 lbs./sq. in. superheated to 750° F., leaving the preheater saturated at 150 lbs./sq. in. Then it is reduced to just above 1 atm., thus re-superheated by expansion. For our purpose it was thought that the heating surfaces of the different components would be sufficient indicators to the relative costs of the different systems. The same general formulæ were employed here as before, and a value of only 5 was given to U when heat is transferred from oil to oil. It will be seen that exchanger No. 2 is really a partial condenser. In designing the condenser for the stripper, U was taken as 20, since the

Table XX.

Heat Exchanger No. 1.

	1 atm. 30° C.	2 atms. 30° C.	4 atms. 30° C.	6 atms. 30° C.	1 atm. −10° C.	1 atm. 0° C.	1 atm. 10° C.	1 atm. 20° C.
Total inlet rate of oil + solute, lbs./hr. . .	198,840	122,840	55,840	49,340	66,840	96,840	126,840	169,840
Temp. rise, °F. . .	108	108	108	108	108	108	108	108
B.Th.U. transmitted/hr.	10.8×10^6	6.6×10^6	3.1×10^6	2.8×10^6	3.6×10^6	5.2×10^6	6.9×10^6	9.2×10^6
Losses B.Th.U./hr. .	0.27×10^6	0.16×10^6	0.08×10^6	0.07×10^6	0.09×10^6	0.13×10^6	0.17×10^6	0.23×10^6
Temp. drop in stripped oil, °F. . . .	112	110	118	122	114	111	113	112
Heating surface, sq. ft. .	4,800	2,940	1,240	1,080	1,440	2,040	2,760	3,660

petrol present will lower it from the accepted value of 25–60 for water condensers. The arithmetic temperature drop was taken throughout instead of the logarithmic mean. The requirements of the different exchangers are given in Tables XX to XXIII.

TABLE XXI.

Steam Preheater for Stripper.

	1 atm. 30° C.	2 atms. 30° C.	4 atms. 30° C.	6 atms. 30° C.	1 atm. −10° C.	1 atm. 0° C.	1 atm. 10° C.	1 atm. 20° C.
Lbs. steam/hr. . .	3,920	2,380	1,150	1,050	1,280	1,870	2,500	3,320
B.Th.U. extracted from steam/hr. . .	800,000	485,000	234,000	214,000	252,000	382,000	510,000	678,000
Temp. rise in oil, °F. .	8	8	8	9	8	8	8	8
Heating surface, sq. ft. .	40	25	12	10	13	19	26	34

TABLE XXII.

Heat Exchanger No. 2.

	1 atm. 30° C.	2 atms. 30° C.	4 atms. 30° C.	6 atms. 30° C.	1 atm. −10° C.	1 atm. 0° C.	1 atm. 10° C.	1 atm. 20° C.
B.Th.U. required to raise the oil from 311° F. to 351° F./hr.	$3{\cdot}94 \times 10^6$	$2{\cdot}42 \times 10^6$	$1{\cdot}08 \times 10^6$	$0{\cdot}95 \times 10^6$	$1{\cdot}3 \times 10^6$	$1{\cdot}90 \times 10^6$	$2{\cdot}50 \times 10^6$	$2{\cdot}76 \times 10^6$
Heating surface, sq. ft. .	800	485	216	190	260	380	500	555

TABLE XXIII.

Condenser for Stripper.

	1 atm. 30° C.	2 atms. 30° C.	4 atms. 30° C.	6 atms. 30° C.	1 atm. −10° C.	1 atm. 0° C.	1 atm. 10° C.	1 atm. 20° C.
Lbs. of steam/hr. entering exchanger No. 2 .	3,920	2,380	1,150	1,050	1,280	1,870	2,500	3,320
Total B.Th.U./hr. in steam above 20° C.	$5{\cdot}33 \times 10^6$	$3{\cdot}22 \times 10^6$	$1{\cdot}55 \times 10^6$	$1{\cdot}42 \times 10^6$	$1{\cdot}73 \times 10^6$	$2{\cdot}51 \times 10^6$	$3{\cdot}38 \times 10^6$	$4{\cdot}50 \times 10^6$
Total B.Th.U./hr. in solute gases above 20° C. entering exchanger No. 2	270,000	270,000	270,000	270,000	270,000	270,000	270,000	270,000
Total B.Th.U./hr. abstracted in exchanger No. 2 .	$3{\cdot}94 \times 10^6$	$2{\cdot}42 \times 10^6$	$1{\cdot}08 \times 10^6$	$0{\cdot}95 \times 10^6$	$1{\cdot}30 \times 10^6$	$1{\cdot}90 \times 10^6$	$2{\cdot}50 \times 10^6$	$2{\cdot}76 \times 10^6$
Total B.Th.U. to be abstracted by condenser/hr.	$1{\cdot}65 \times 10^6$	$1{\cdot}07 \times 10^6$	$0{\cdot}74 \times 10^6$	$0{\cdot}74 \times 10^6$	$0{\cdot}70 \times 10^6$	$0{\cdot}88 \times 10^6$	$1{\cdot}15 \times 10^6$	$2{\cdot}01 \times 10^6$
Heating surface, sq. ft. .	3,860	2,940	1,680	1,680	1,590	2,000	2,650	4,770
Lbs. cooling water/hr. (45° F.–190° F.) .	11,400	7,400	5,100	5,100	4,850	6,100	7,900	13,800

Cold Exchanger for Stabilizer.—The oil entering the stabilizer in the compression system is at 30° C., but not so in the refrigeration system. To bring it up to this temperature a heat exchanger was put here to accomplish the double purpose of this and cooling the stripped oil simultaneously. It is shown in Table XXIV.

TABLE XXIV.

	1 atm. −10° C.	1 atm. 0° C.	1 atm. 10° C.	1 atm. 20° C.
B.Th.U. required/hr. . .	$2{\cdot}50 \times 10^6$	$2{\cdot}61 \times 10^6$	$2{\cdot}28 \times 10^6$	$1{\cdot}53 \times 10^6$
Heating surface, sq. ft. . .	420	530	460	330

Cooler for Stripped Oil.—The stripped oil must be brought to the temperature operating in the absorber. The cooler here (Table XXV) is designed to do this except for the systems working at and below 10° C., where a refrigerating component is necessary.

TABLE XXV.

	1 atm. 30° C.	2 atms. 30° C.	4 atms. 30° C.	6 atms. 30° C.	1 atm. −10° C.	1 atm. 0° C.	1 atm. 10° C.	1 atm. 20° C.
B.Th.U. extracted/hr. .	16×10^6	$9{\cdot}75 \times 10^6$	$4{\cdot}3 \times 10^6$	$3{\cdot}6 \times 10^6$	$0{\cdot}84 \times 10^6$	$1{\cdot}25 \times 10^6$	$1{\cdot}6 \times 10^6$	$1{\cdot}5 \times 10^6$
Cooling surface, sq. ft. .	6,670	4,050	1,790	1,500	1,120	1,670	2,140	1,580
Lbs. water/hr. . .	96,000	58,000	26,000	22,000	5,000	7,500	9,600	9,000

Refrigerators. We need two sets of refrigerators: the first for chilling the oil and the second for the feed gas. Tables XXVI and XXVII give the requirements of these.

TABLE XXVI.

	1 atm. −10° C.	1 atm. 0° C.	1 atm. 10° C.
Lbs. oil circulated/hr.	65,000	95,000	125,000
Temp. of exit oil, °F.	14	32	50
B.Th.U. removed/hr.	$1{\cdot}56 \times 10^6$	$1{\cdot}33 \times 10^6$	$0{\cdot}625 \times 10^6$

TABLE XXVII.

Pressure of exit gas, lbs./sq. in. .	15	15	15	15
Temperature of exit gas, °C. . .	−10	0	10	20
Lbs. gas/hr.	14,438	14,438	14,438	14,438
Temp. drop from 86° F., °F. . .	72	54	36	18
B.Th.U. removed/hr. . . .	520,000	390,000	360,000	130,000
Cu. ft. (atm. and 30° C.) passing/hr. .	208,333	208,333	208,333	208,333

The next main section of auxiliaries deals with the tanks necessary. A short description follows:

Gas Holder.—This is the same for all cases. Its capacity is that of the gas passing in approximately 30 minutes—100,000 cu. ft.

Reserve Tank for Oil should be installed in the refinery, and its cost will be on the refinery estimate of the company concerned. Hence we need not account for it in this paper. The pump, however, should be put on the absorption plant cost.

Stand-by Tanks.—There are three of these in each plant: one after the absorber, one after the stabilizer and the third after the stripper, in the oil circuit. They need only hold oil flowing from 10 to 20 minutes, to allow the attendants to shut down the plant in case of a breakdown. Therefore one capacity will serve for all—*i.e.* diameter 10 ft.; height 8 ft. But they must withstand their operating pressures.

Water Separators.—This is an empty tank with an exit valve at the bottom for the water and one near the top for the petrol. The mixture enters near the middle. The level of the water is kept at the level of entrance automatically. This separator need hold only a five minutes flow, since water

and gasoline separate easily. For all systems we will have: diameter 1 ft. 6 in.; height 10 ft.

Petrol Receiver.—This again need not be different for the different systems, since the extracted gasoline per hour is nearly constant for all. It will store about 6 hours production or 8000 lbs. A tank of 6 ft. diameter and 6 ft. high is adequate.

Water Receiver.—This would be a part of the power plant, since this water will be used in cooling towers or for some other purpose, where the fact that it has a little gasoline in it is neither objectionable nor dangerous.

The final important item in the auxiliaries of the plant that we are to describe briefly deals with the compressor and pumps necessary for the plant. Table XXVIII gives the specifications for the compressor, which should be fitted with interstage coolers and an external cooler to abstract the heat of compression and keep the temperature of the feed to the absorber at 30° C.

TABLE XXVIII.

Temperature of exit gas, °C. . . .	30	30	30
Pressure of exit gas, lbs./sq. in. . .	30	60	90
Cu. ft. of gas at 1 atm. and 30° C. entering/hr.	210,000	210,000	210,000

The pumps will be of the centrifugal type coupled to electric motors. Table XXIX gives the specifications for each pump and motor required.

TABLE XXIX.

	1 atm. 30° C.	2 atms. 30° C.	4 atms. 30° C.	6 atms. 30° C.	1 atm. −10° C.	1 atm. 0° C.	1 atm. 10° C.	1 atm. 20° C.
Pump No. 1.								
Capacity, galls./min. .	380	250	120	95	135	190	250	340
H.P. of pump . .	12	10	8	9	3	4	5	9
H.P. of motor . .	18	15	12	14	5	6	7	14
Pump No. 2.								
Capacity, galls./min. .	380	250	120	95	135	190	250	340
H.P. of pump . .	45	24	10	6	18	24	30	40
H.P. of motor . .	70	36	15	9	27	36	45	60
Working pressure, atms.	8·6	8·6	8·6	8·6	8·6	8·6	8·6	8·6
Working temp., °C. .	30	30	30	30	−10	0	10	20
Pump No. 3.								
Capacity, galls./min. .	380	250	120	95	135	190	250	340
H.P. of pump . .	6	5	3	2	3	3	5	6
H.P. of motor . .	9	8	5	3	5	5	8	9
Working pressure, atm. .	1	1	1	1	1	1	1	1
Working temp., °C. .	182	182	182	182	182	182	182	182
Pump No. 4.								
Capacity, galls./min. .	380	250	120	95	135	190	250	340
H.P. of pump . .	2	2	1	1	3	3	3	2
H.P. of motor . .	3	3	2	2	5	5	5	3
Working pressure, atm. .	1	1	1	1	1	1	1	1
Working temp., °C. .	125	125	125	125	125	125	125	125

Pump No. 5 is a 2-horse-power pump, and is satisfactory for all systems. Pump No. 6 is a 1-horse-power pump, working at 23° C. and 8·6 atms. The motors for these pumps should be of 3 and 1½ horse power respectively. The size of the pumps for driving water through the condensers and coolers will, of course, depend on the locality; but they would not generally be large except in cases where water is at a distance or in deep wells, which latter cases we will not presume.

The fixtures and accessories, with all the measuring apparatus and valves, pipes, etc., will be taken into account in a general way as a percentage of the total cost.

Costing.

This part of the problem is the most difficult to assess, since, for obvious reasons, the information given in the literature about the £ *s*. *d*. value of plants is scanty. However, such scanty information enabled the writer to compile the following tables. These are by no means very reliable bases for the absolute values of the different items; but it is claimed that they show the *relative* values with reasonable accuracy.

Tables XXX and XXXI show the individual and total costs of the most important items of the eight different plants investigated. The figures obtained here are used as the basis for estimating the capital cost of the different systems.

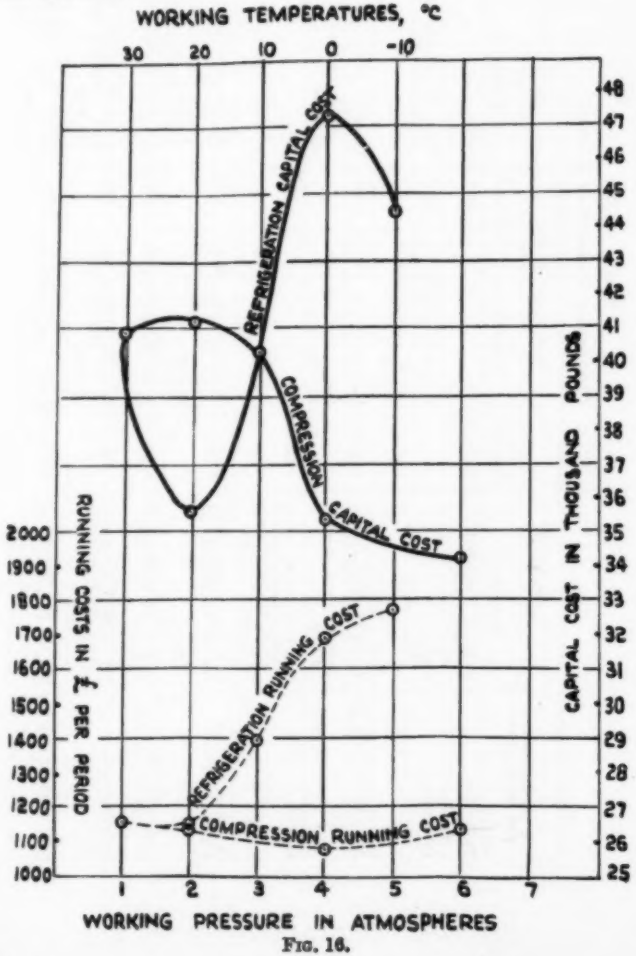


Fig. 16.

TABLE XXX.

Compression System Cost Estimate.

Working Pressures and Temperatures.	1 atm. and 30° C.		2 atms. and 30° C.		4 atms. and 30° C.		6 atms. and 30° C.	
	Description.	Cost, £.	Description.	Cost, £.	Description.	Cost, £.	Description.	Cost, £.
Gas holder.	Capacity: 100,000 cu. ft., 1 atm., 30° C.	9,000	Same.	9,000	Same.	9,000	Same.	9,000
Compressor.	None.	—	Gas rate of 210,000 cu. ft./hr. at 1 atm. and 30° C. compressed to 2 atms. and 30° C.	8,000	Same rate of gas compressed to 4 atms. and 30° C.	9,000	Same rate of gas compressed to 6 atms. and 30° C.	9,000
Absorber.	5 ft. 0 in. in dia., 46 ft. 0 in. in height, 20 plates; working under 1 atm.	1,700	4 ft. 3 in. in dia., 42 ft. 0 in. in height, 18 plates; working under 2 atms.	1,200	3 ft. 9 in. in dia., 34 ft. 0 in. in height, 14 plates; working under 4 atms.	800	3 ft. 3 in. in dia., 30 ft. 0 in. in height, 12 plates; working under 6 atms.	700
Stabilizer.	1 ft. 6 in. in dia., 26 ft. 0 in. in height without kettle, 17 plates; working under 8·6 atms.	240	Same.	240	Same.	240	Same.	240
Strippers (two in series, each).	3 ft. 0 in. in dia., 32 ft. 0 in. in height, 14 plates; working at 182° C.	1,100	2 ft. 3 in. in dia., 36 ft. 0 in. in height, 16 plates; working at 182° C.	900	1 ft. 9 in. in dia., 36 ft. 0 in. in height, 16 plates; working under 182° C.	850	1 ft. 6 in. in dia., 32 ft. 0 in. in height, 14 plates; working at 182° C.	800
Lean oil cooler.	6670 sq. ft. cooling surface.	5,000	4050 sq. ft. cooling surface.	3,500	1790 sq. ft. cooling surface.	1,500	1500 sq. ft. cooling surface.	1,300
Stabilizer kettle.	830 sq. ft. heating surface; working under 8·6 atms.	650	535 sq. ft. heating surface; working under 8·6 atms.	400	260 sq. ft. heating surface; working under 8·6 atms.	280	250 sq. ft. heating surface; working under 8·6 atms.	280
Heat exchanger No. 1.	4800 sq. ft. heating surface; working at 180° C. and 8·6 atms.	4,000	2940 sq. ft. heating surface; same working conditions.	2,500	1240 sq. ft. heating surface; same working conditions.	950	1080 sq. ft. heating surface; same working conditions.	900

Heat exchanges No. 2.	800 sq. ft. heating surface; working under 8 atms. and 180° C.	640	485 sq. ft. heating surface; under same conditions.	350	216 sq. ft. heating surface; under same conditions.	290	190 sq. ft. heating surface; under same conditions.	250
Steam preheater.	40 sq. ft. heating surface, 240 lbs. steam.	40	25 sq. ft. heating surface, 240 lbs. steam.	30	12 sq. ft. heating surface, 240 lbs. steam.	25	10 sq. ft. heating surface, 240 lbs. steam.	25
Condensers: (*a*) For propane.	One working at 8·6 atms., having 275 sq. ft. cooling surface.	300	Two working under same conditions, each having 210 sq. ft. cooling surface.	450	One working under same conditions, having 350 sq. ft. heating surface.	325	Two working under same conditions, each having 250 sq. ft. cooling surface.	500
(*b*) For gasoline.	3860 sq. ft. cooling surface.	3,500	2940 sq. ft. cooling surface.	2,000	1680 sq. ft. cooling surface.	1,200	1680 sq. ft. cooling surface.	1,200
Tanks: (*a*) Lean oil tank.	10 ft. in dia., 8 ft. in height; working at 1 atm.	70	Same size, storing oil at 2 atms.	70	Same size, storing oil at 4 atms.	80	Same size, storing oil at 6 atms.	80
(*b*) Rich oil tank from absorber.	10 ft. in dia., 8 ft. in height.	70	Same size, storing oil at 2 atms.	70	Same size, storing oil at 4 atms.	80	Same size, storing oil at 6 atms.	80
(*c*) Rich oil tank from stabilizer.	10 ft. in dia., 8 ft. in height; oil at 100° C. and 9 atms.	90	Same.	90	Same.	90	Same.	90
(*d*) Water separator.	1 ft. 6 in. in dia., 10 ft. in height.	15	Same.	15	Same.	15	Same.	15
(*e*) Petrol receiver.	6 ft. in dia., 6 ft. in height.	40	Same.	40	Same.	40	Same.	40
Pumps: No. 1. No. 2. No. 3. No. 4.	Table XXIX. " " " " " "	900	Same Table. " " " " " "	850	Same Table. " " " " " "	800	Same Table. " " " " " "	750
Total cost of main part.		27,355		29,705		25,565		24,840

TABLE XXXI.

Refrigeration System Cost Estimate.

Working Pressures and Temperatures.	15 lbs./sq. in. and −10° C.		15 lbs./sq. in. and 0° C.		15 lbs./sq. in. and 10° C.		15 lbs./sq. in. and 20° C.	
	Description.	Cost, £.	Description.	Cost, £.	Description.	Cost, £.	Description.	Cost, £.
Gas holder.	Capacity: 100,000 cu. ft., 1 atm., 30° C.	9,000	Same.	9,000	Same.	9,000	Same.	9,000
Refrigerators (*a*) Inlet gas.	Extracts 520,000 B.Th.U./hr.; gas rate 220,000 cu. ft./hr.; initial temp. 30° C.; initial press. 1 atm.; final temp. −10° C.	15,000	Extracts 390,000 B.Th.U./hr.; gas rate 220,000 cu. ft./hr.; initial temp. 30° C.; initial press. 1 atm.; final temp. 0° C.	13,800	Extracts 260,000 B.Th.U./hr.; gas rate 220,000 cu. ft./hr.; initial temp. 30° C.; initial press. 1 atm.; final temp. 10° C.	7,000	Extracts 130,000 B.Th.U./hr.; gas rate 220,000 cu. ft./hr.; initial temp. 30° C.; initial press. 1 atm.; final temp. 20° C.	1,000
(*b*) Lean oil.	Extracts $1{\cdot}6 \times 10^6$ B.Th.U./hr.; oil rate 65,000 lbs./hr.; final temp. −10° C.		Extracts $1{\cdot}5 \times 10^6$ B.Th.U./hr.; oil rate 95,000 lbs./hr.; final temp. 0° C.		Extracts $0{\cdot}7 \times 10^6$ B.Th.U./hr.; oil rate 125,000 lbs./hr.; final temp. 10° C.		None.	
Absorber.	4 ft. 6 in. in dia., 34 ft. 0 in. in height, 14 plates (−10° C.).	1,000	4 ft. 6 in. in dia., 40 ft. 0 in. in height, 17 plates (0° C.).	1,200	4 ft. 6 in. in dia., 42 ft. 0 in. in height, 18 plates (10° C.).	1,300	4 ft. 9 in. in dia., 46 ft. 0 in. in height, 20 plates.	1,600
Stabilizer.	1 ft. 6 in. in dia., 26 ft. 0 in. in height, without kettle, 17 plates; working under 8·6 atms.	240	Same.	240	Same.	240	Same.	240
Strippers (2 in series, each).	1 ft. 6 in. in dia., 32 ft. 0 in. in height, 14 plates; 182° C. working temperature.	800	2 ft. 0 in. in dia., 28 ft. 0 in. in height, 12 plates; 182° C. working temperature.	800	2 ft. 6 in. in dia., 36 ft. 0 in. in height, 16 plates; 182° C. working temperature.	900	2 ft. 9 in. in dia., 32 ft. 0 in. in height, 14 plates; 182° C. working temperature.	1,000
Lean oil cooler.	1120 sq. ft. cooling surface.	900	1670 sq. ft. cooling surface.	1,400	2140 sq. ft. cooling surface.	1,850	1580 sq. ft. cooling surface.	1,250
Cold exchanger.	420 sq. ft. cooling surface.	320	530 sq. ft. cooling surface.	400	460 sq. ft. cooling surface.	330	330 sq. ft. cooling surface.	300

Stabilizer kettle.	310 sq. ft. heating surface; 8·6 atms. working pressure.	300	430 sq. ft. heating surface; 8·6 atms. working pressure.	350	540 sq. ft. heating surface; 8·6 atms. working pressure.	400	725 sq. ft. heating surface; 8·6 atms. working pressure.	600
Heat exchanger No. 1.	1440 sq. ft. heating surface; working at 180° C. and 8·6 atms.	1,400	2040 sq. ft. heating surface; same working conditions.	1,900	2760 sq. ft. heating surface; same working conditions.	2,200	3660 sq. ft. heating surface; same working conditions.	2,600
Heat exchanger No. 2.	260 sq. ft. heating surface; working at 180° C. and 8 atms.	250	380 sq. ft. heating surface; same working conditions.	310	500 sq. ft. heating surface; same working conditions.	375	555 sq. ft. heating surface; same working conditions.	400
Steam preheater.	13 sq. ft. heating surface, 240 lb. steam.	30	19 sq. ft. heating surface, 240 lb. steam.	30	26 sq. ft. heating surface, 240 lb. steam.	30	34 sq. ft. heating surface, 240 lb. steam.	30
Condensers (*a*) For propane.	One working at 8·6 atms. having 350 sq. ft. cooling surface.	325	Two working under 8·6 atms. having 200 sq. ft. cooling surface each.	450	Two same.	450	Two same.	450
(*b*) For gasoline.	1590 sq. ft. cooling surface.	1,250	2000 sq. ft. cooling surface.	1,850	2650 sq. ft. cooling surface.	2,150	4770 sq. ft. cooling surface.	4,000
Tanks: (*a*) Lean oil tank.	10 ft. in dia., 8 ft. in height, at −10° C.	70	Same size, storing oil at 0° C.	70	Same size, storing oil at 10° C.	70	Same size, storing oil at 10° C.	70
(*b*) Rich oil tank from absorber.	10 ft. in dia., 8 ft. in height.	70	Same.	70	Same.	70	Same.	70
(*c*) Rich oil tank from stabilizer.	10 ft. in dia., 8 ft. in height; oil at 100° C. and 9 atms.	90	Same.	90	Same.	90	Same.	90
(*d*) Water separator.	1 ft. 6 in. in dia., 10 ft. in height.	15	Same.	15	Same.	15	Same.	15
(*e*) Petrol receiver.	6 ft. in dia., 6 ft. in height.	40	Same.	40	Same.	40	Same.	40
Pumps and motors: No. 1.	Table XXIX.	700	Same Table.	750	Same Table.	800	Same Table.	850
No. 2.	" "		" "		" "		" "	
No. 3.	" "		" "		" "		" "	
No. 4.	" "		" "		" "		" "	
Total cost of main parts.		30,900		32,765		27,310		23,605

Table XXXII gives the final capital cost of the plants for the different systems. These values are plotted on Fig. 16, see page 101.

TABLE XXXII.

System.	1 atm. 30° C. £	2 atms. 30° C. £	4 atms. 30° C. £	6 atms. 30° C. £	1 atm. −10° C. £	1 atm. 0° C. £	1 atm. 10° C. £	1 atm. 20° C. £
Cost of main parts .	27,355	29,705	25,565	24,840	30,900	32,765	27,310	23,605
Lagging and other precautions . . .	1,600	1,400	1,200	1,000	1,000	1,200	1,400	1,600
Pipes and valves (10%).	2,735	2,970	2,556	2,484	3,090	3,276	2,731	2,360
Instruments, etc. . .	1,200	1,200	1,200	1,200	1,000	1,000	1,000	1,000
Structure and foundations . . .	1,000	900	800	700	800	850	900	950
	33,890	34,175	29,321	28,224	36,790	39,141	33,341	29,515
Contingencies (10%) .	3,389	3,417	2,932	2,822	3,679	3,914	3,334	2,951
	37,279	37,592	32,253	31,046	40,469	43,055	36,675	32,466
Erection charges (10%) .	3,728	3,759	3,225	3,104	4,047	4,305	3,667	3,246
Total (say). .	41,000	41,350	35,480	34,250	44,520	47,360	40,340	35,710

Fig. 16 shows us the fact that, in the case of the compression system, there is a maximum value for capital cost at 2 atms., after which there is a rapid drop in cost until about 4 atms., when the capital cost curve tends to flatten out. The reason for this is obvious. The small rise at the beginning is due to the fact that while compression to 30 lbs./sq. in. in the absorber reduces the general dimensions of the whole plant, thus bringing down their prices, the cost of the compressor itself and the extra cost of the components which have to stand pressure counterbalance this gain. These two variables, one tending to increase, the other to decrease the price of the plant, just equalize at a working pressure of approximately 2·25 atms. After that the economy due to compression gets the upper hand. But it is clear that it is not advantageous to go beyond, say, 4 atms., since the extra economy becomes proportionately less and less beyond this point.

The graph for the refrigeration systems presents quite the opposite story. There is a minimum value for cost at 20° C., then a sharp rise until 0° C. when the value again falls. The last part is not really accurate. The cost at 0° C. and below it should be higher than shown, since some water-separating plants should be installed. These are to take the water both from the gases and the oil, lest it freezes in the pipes and other parts, thus stopping the operation of the plant. They were not included here, since it is clear that even without them the initial cost (and operating costs, as we shall see) is too prohibitive to allow us to entertain the idea of using one of these systems.

It is expected that the cost of the plant working at 20° C. should be a minimum, since no refrigeration plant was incorporated. It will be remembered that only water cooling was employed. Thus with no compressor, nor a refrigerator, except for the gas, the system is equivalent in cost to one working under 4 atms. Hence purely from the point of view of cost, it is concluded that a system working under 1 atm. and 20° C. absorber pressure and temperature would best suit us.

The question arises whether a "combination system"—*i.e.* one working at some optimum values of temperatures and pressures—is economical to

install. Evidently if our combination system includes both a refrigerator and a compressor, it will be much more expensive than a "simple" plant. Hence, we would take 20° C. as our minimum temperature. Let us then compress the gas to 3·5 atms. It is then, in fact, a compression system with only the initial temperature brought down by 10° C. This will mean a smaller L/G ratio used. If we plot cost of plant for the different compression systems against L/G ratio used in each (Fig. 17), we get a very smooth curve for systems working under different pressures and at 30° C.

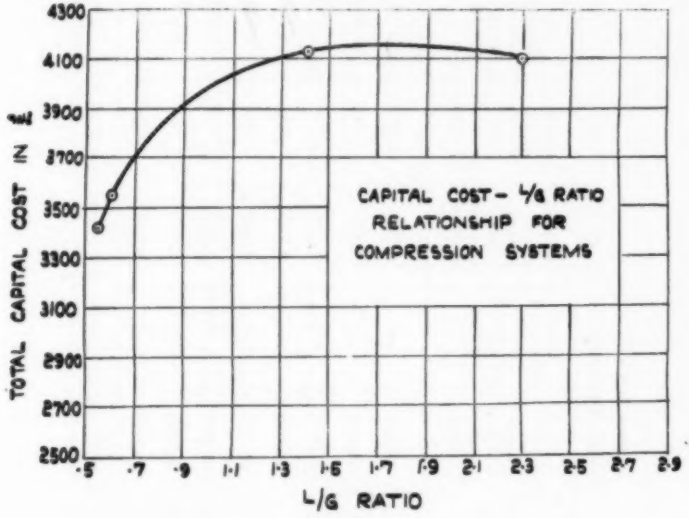


FIG. 17.

Under "Conclusions on Absorber Design" we found (fourth point) that "between 1 and 4 atms. and — 10° C. and + 30° C., 1° C. decrease in temperature has approximately the same effect as 1·12 lbs./sq. in. increase in pressure." This means that, taking an absorber of a given number of plates, we will require the same L/G ratio for working at 20° C. and 3·5 atms. as for a system working at 30° C. and 4·25 atms. These two systems, then, would have approximately the same capital cost, since there is a direct relationship between L/G ratio and capital cost for all compression systems. (It is important that no refrigerator be incorporated into the plant, since L/G—cost curve is then entirely different.) Thus we see that our new combination system will cost £35,000, while a "simple" system working at 20° C. and no compression costs £35,700. The accuracy of our work does not warrant the statement that there is a real difference. Hence combination systems, as far as our problem is concerned, failed us, since the best of them had no special recommendations.

For calculating operating costs Table XXXIII gives the process requirements for the eight different systems. Most of the columns are merely the additive results from previous columns; but in estimating the power for

TABLE XXXIII.

Process Requirements.

Working Conditions.	Petrol Receiver, tons/ period of 28 days.	Oil Used, ton/hr.	Power for Compressor, kw.h./ period of 28 days.	Power for Refrigerator, kw.h./ period of 28 days.	Power for Pumps, kw.h./ period of 28 days.	Heat Removed by Refrigerator, million B.Th.U. per hr.	150 lbs./ sq. in. Steam, tons/ period of 28 days.	240 lbs./ sq. in. Steam, tons/ period of 28 days.	Cooling Water, tons/ period.	Steam Water Regained at 100° C., tons/ period.	Labour, number of men per shift.
1 atm. and 30° C. .	550	88·8	—	—	59,000	—	3,720	1,180	35,600	32,500 *	4
2 atms. and 30° C. .	,,	54·0	127,925	—	34,000	—	2,400	710	20,400	19,900 *	4
4 atms. and 30° C. .	,,	23·2	255,000	—	20,500	—	1,110	350	10,100	9,000 *	4
6 atms. and 30° C. .	,,	21·2	327,675	—	18,600	—	1,110	320	9,350	7,500 *	4
1 atm. and −10° C.	,,	29·0	—	1,120,000	23,000	2·08	1,350	385	3,800	1,350	4
1 atm. and 0° C. .	,,	42·4	—	920,000	28,000	1·72	1,900	560	4,900	1,900	4
1 atm. and 10° C. .	,,	56	—	476,000	34,600	0·89	2,450	750	6,150	2,450	4
1 atm. and 20° C. .	,,	75·2	—	69,500	46,000	0·13	3,150	990	7,750	3,150	4

* Water used in the oil cooler is included here; in the refrigeration system this water is not at 100° C., so it was excluded. The water condensing the petrol in the strippers condenser is useless for generating steam—hence it is not included in the estimate.

TABLE XXXIV.

Running Costs in £/Period of 28 Days.

Pressure and Temp.	NH_3 Make up.	Electric Power.	Steam, H.P. + L.P.	Cooling Water.	Regained Steam Water at 100° C.	Labour.	Process Supervision.	Research Charges.	Instruments, Labs., etc.	Repairs.	Obsolescence.	Rates and Insurance.	Works Gen. Charges.	Total.
1 atm. and 30° C. .	—	49·0	373·5	35·6	−81·3	180·0	72·0	125·0	45·0	136·0	170·0	27·3	27·5	1159·6
2 atms. and 30° C. .	—	135·0	234·6	20·4	−50·0	,,	,,	,,	,,	148·0	172·0	29·7	,,	1139·2
4 atms. and 30° C. .	—	229·0	111·2	10·1	−22·5	,,	,,	,,	,,	127·0	152·0	25·5	,,	1081·8
6 atms. and 30° C. .	—	288·5	107·9	9·4	−18·6	,,	,,	,,	,,	124·0	148·0	24·8	,,	1133·5
1 atm. and −10° C.	0·5	953·0	130·4	3·8	− 3·4	,,	,,	,,	,,	97·0	121·0	19·4	,,	1771·2
1 atm. and 0° C. .	0·3	790·0	186·0	4·9	− 4·8	,,	,,	,,	,,	109·0	137·0	21·9	,,	1693·8
1 atm. and 10° C. .	0·2	425·0	242·5	6·2	− 6·1	,,	,,	,,	,,	115·0	144·0	23·0	,,	1399·3
1 atm. and 20° C. .	0·2	96·3	315·0	7·8	− 7·9	,,	,,	,,	,,	118·0	148·0	23·6	,,	1150·5

the compressors they were assumed to have 75 per cent. isothermal, 91 per cent. mechanical and 90 per cent. electrical efficiencies. In the case of the refrigerators 45 per cent., 91 per cent. and 90 per cent. were taken as those obtainable on commercial plants of this size.

The following rates were assumed in constructing Table XXXIV.

Electrical power	at 0·2*d.*/kw.hr.
Cooling water (from river) .	at 0·24*d.*/ton.
Steam	at 0·1*d.*/kw.hr.
	(1 Tonne H.P. = 274 kw.hr.
	1 „ L.P. = 158 kw.hr.)
Steam water . . .	at 0·6*d.*/ton
	(in our case on the profit side).
Process supervision . .	40% labour cost.
Research charges . . .	same for all.
Instruments, laboratories, etc..	25% labour cost.
Labour	£15/man/period.
Repairs (per period) . .	0·5% on capital value.
Obsolescence (per period) .	0·5% on capital value + 0·25% on building, etc.
Rates and Insurance . .	0·10% on plant value.
Works general charges . .	12·5% process wages.

Plotting the running costs in pounds per period of 28 days, we find that the compression system has a minimum value at 4 atms. absorber pressure. This is about the same pressure as that which gives the best results from capital cost point of view. Hence, should we decide upon a compression system, it is quite definite that an absorber pressure of 4 atms. is the least expensive method of attaining our requirements. (See Fig. 16.)

In the case of the refrigeration system the running costs fall to the value obtained at 20° C.—£1150/period—and then rise steeply. They behave just like the capital costs, and for the same reasons. It may be mentioned again that running costs at and below 0° C. are much more than they appear here, due to the necessity of installing and running water-separating plants.

As the best combination system was equivalent, approximately, to a compression system of 4 atms., we will discuss it with few words. At best its running cost will be equivalent to that of the latter, while the fact that we have to refrigerate the gas and cool the oil through 10 extra degrees tends to increase expenditure.

Hence the choice lies between a plant running at 20° C. and 1 atm. and one at 30° C. and 4 atms. Table XXXV compares these two plants.

TABLE XXXV.

System.	Capital Cost.	Running Cost.
4 atms. and 30° C.	£35,480	£1081·8/period
1 atm. and 20° C.	£35,710	£1150·5/period
Difference in favour of 4 atms. and 30° C. .	£230	£68·7/period

It is the author's opinion that, as far as the capital cost is concerned, there is no practical difference in favour of either. But there is a difference

of approximately 6 per cent. in the running costs in favour of the compression system. Against this stand: (1) our assumptions were made in order to ensure an accuracy of $\pm$ 5 per cent.; (2) natural preference for a plant working under 1 atm. to one working under 4 atms.

Conclusions.

One of the aims of this paper was to show that there are limits for pressures and temperatures to be employed, below and beyond which we incur extra and unnecessary expenses. In this specific case, we find that these two limits require practically the same expenditure. The author is of the opinion that the refrigeration system, working under 20° C. and 1 atm. is to be preferred, despite the slight increase in calculated expenses. It is put forward as the best compromise between easy running and expense. "... it must be remembered" as a better engineer than the author has recently put it, "that engineering in all its phases is a matter for compromise, and it is not always possible to have everything as one would like it."

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Department of Oil Engineering and Refining,
The University,
Edgbaston, Birmingham.

DEEP PUMPING WELLS.*

By E. Boaden, B.Sc. (Member).

Synopsis.

The gaslift stage in the producing life of a well may often be eliminated by the earlier installation of pumping equipment.

The choice of equipment must be guided by the individual case. Wells of depth below 1000 meters are considered, with particular reference to Roumanian conditions, and the advantages and disadvantages of the different types of central powers and individual units are discussed.

Methods of estimating the available quantity of fluid to be pumped and the various combinations of tubing, rods and pumps to handle these quantities are considered. Notes are given on rod stretch, polish-rod, loads and dynamic loads. The importance of correct counterbalancing is stressed and the power required to take care of the loads, taking transmission losses into account, is considered.

Useful practices in the setting of pumps are indicated, together with notes on subsurface and surface equipment. Methods of solving paraffin troubles tried out in Roumania are examined, and a recommendation is made. A case is cited of a well producing quantities of salt water accompanied by a small percentage of oil at a cost comparing favourably with previous gaslift operation cost. Some points in connection with economies to be made in the servicing of pumps and in the running of a pumping lease are shown.

In conclusion, it is thought that there are no insurmountable difficulties in the way of pumping most wells at present producing in Roumania.

When in the past we have surveyed our producing well reports and note the falling off in production of some of our flowing wells, our minds have usually turned to the list of available compressors, and our activities to the hurried rigging up of these compressors on expensive concrete foundations, housed in expensive sheds and hooked up to expensive networks of lines and distributors. After a year or two, again noting the falling production of our gaslift wells, the high quantity of input gas and its cost, we again direct our energies to expensive concrete foundations and sheds, but this time for the purpose of mounting pumping rigs of some kind.

Except in certain cases where large liquid volumes, high gas–oil ratios or sandy conditions are involved, it is likely that the gaslift stage can in the future be cut out and most wells put on the pump immediately they cease flowing. This is general practice in some foreign fields, and will doubtless become general practice in some fields in this country.

What we should be likely to need is a moderate-capacity compressor installation to temporarily lift wells coming off natural flow until such time as pumping installations can be rigged up, since, in the usual course of events, only one or two wells cease natural flow at any one time.

The turning over of wells to pumping may often be delayed if high-pressure gas is available at low cost from some well in the district.

* Paper read at a General Meeting of the Roumanian Branch held at the Ploesti Chamber of Commerce, on October 14th, 1937.

In this country the majority of Meotic wells flow until their production falls to less than four cars a day and it is likely that most of these could be produced by agitating immediately after ceasing to flow, gradually becoming straight pumpers.

Pumping Equipment.

The choice of kind of pumping equipment to instal is not easy, and at present in this country depends largely on what is available, what can be made up or manufactured locally and on the possibility of importing from different manufacturing countries. This latter factor makes the standardization of pumping installations extremely difficult, since what is available for purchase to-day is no longer available to-morrow. For the purpose of this paper we will consider only wells having a depth of over 1000 metres.

For groups of wells, the central power must always be considered, although the practical well depth which these will serve should not be more than about 1200 metres, and at such depths it is not likely that more than six wells can be handled efficiently on full-time pumping, unless they are extremely steady pumpers with little off time and well balanced.

In very shallow fields the number of wells handled by a big central power seems to be dependent only on the ingenuity displayed in the layout of the pull-rod lines and in the correct balancing and programming of shut-down times.

Central Installations.

The two types of central installations, the band-wheel and the geared, each have their advantages and disadvantages. The band-wheel has a higher installation cost, needs more foundations and floor space, and must be housed; on the other hand the author considers that it has a longer life. The band-wheel type of installation costs about 30 per cent. more than its equivalent geared type. Central powers are made up to a capacity of 100 H.P. with strokes up to 91 cm. or 36 in. There is usually a maximum unbalanced load recommended by the makers, which it is not safe to exceed.

An inherent disadvantage of all central powers is the lack of flexibility in both speed and stroke. Stroke can be multiplied in several well-known ways, but in heavy wells any change in stroke must be compensated by adjustment of counterbalance around the power, which operation can cause considerable work, until all wells have settled down to steady production. Where double-throw cranks or eccentrics giving different stroke lengths are fitted, the counterbalancing needs even more frequent adjustment.

Action may be transmitted to the polished rod via pull-rods, through beam, jack or by means of sprocket and chain. The sprocket-and-chain method is cheap to instal, since old rotary material may be used, but it is doubtful if the economy in initial installation is justified, since this form of transmission can cause considerable shut-down time on heavy wells. Regarding counterbalancing, the wells are first counterbalanced against each other, and the resultant is counterbalanced against jack- or pit-type counterbalances provided around the power. Too much counterbalance

cannot be profitably applied at the well, since this results in sag and snatching of the pull-rod lines.

The design of long pull-rod lines is important, since the use of undersized rods can result in a big loss of stroke—one case of a group of four wells having an average polish-rod load of 6½ tons and running on ⅞-in. rod lines of lengths varying from 150 to 250 metres showed that the 90-cm. stroke at the power was reduced from 4 cm. to 8 cm. or from 4½ to 9 per cent. at the wells, with a corresponding loss of possible volume pumped.

Experiments carried out in the U.S. have shown that loss of stroke and power on pull-rod lines can be reduced by the provision of rotating rod-line carrier heads instead of the old type wooden doll heads, and by the arrangement of the carrier heads to follow the natural catenary curve or sag of the line under maximum load.

Individual Units.

On balance, the author considers that most wells over 1000 metres deep can be better handled by the use of individual units than by the use of a central power, since at such wells, even though pump depth and production pumped may not vary greatly from well to well, individual loads may be very different, due to crooked holes and a multitude of other causes. The choice of individual unit must always be guided in the first place by the expected load and volume, and afterwards by considerations regarding pulling equipment and accessibility.

A decision must be taken whether some type of portable hoist is available for pulling work, whether separate hoisting equipment is to be provided at each well, or whether individual hoisting equipment is to be incorporated in the pumping installation. In this country most companies have had available slow-running gas engines of 40–60 H.P. still capable of years of service, together with numbers of bailing drums of various types.

It has been possible to utilize these in making up complete individual well installations with pulling unit at small cost, and they give very satisfactory service within their limitations, the limiting factor being belt slippage, which, beyond a certain value of unbalanced load, begins to give trouble.

The gas engine is arranged to drive a countershaft through belting from which there are two belt drives, one to the hoisting unit provided with a clutch, and the second, also provided with a clutch, to the crankshaft. A standardized steel walking beam and pitman provided with cast-iron counterweights completes the installation. The maximum practical stroke is 2 metres. It is to be noted that the salvage value of such an installation is considerably lower than that of a reduction gear unit of the same capacity. As an example of the kind of well such a unit can handle, the author can cite one pumping 7 tons from a depth of 2200 metres, with a 2-in. rod liner pump with plunger diam. 1¼ in., on a combination string of ⅞-in. and ¾-in. rods at 12–1^{80} m. strokes/minute, which is counterweighted sufficiently to cause no appreciable belt slip. The maximum polish-rod load is about 9 tons,

During late years a system of back crank pumping has been developed

in the U.S.A., and has been followed to some extent in this country. The method consists of utilizing the counterweighting effect necessary to balance a well for pumping a second or more wells.

The pumping unit is fitted with a second crank, which is mounted on the crankshaft at 90 degrees to the main crank, and this second crank operates the pull rods actuating the second well. A counterbalancing system has to be provided in case one of the wells is off the pump, and this can be so arranged as to take the place of either well in its off time. This system has been used to operate wells with pump run to 1700 metres, where it has been possible to arrange good counterbalancing and having a maximum polish-rod load of 7 tons. It, however, suffers from the same disadvantages as the central power as regards inelasticity of stroke and speed.

When applied to a pair of wells with differing polish-rod loads, the best practice is to mount the unit at the heavier well and pump the lighter from the back crank. In this system the initial investment is somewhat lower, but the running and supervision costs are certainly higher than in the case of individually powered wells.

When separate hoisting equipment or a portable hoist is available, the best all-round equipment to use is one of the many good makes of reduction unit actuated by electric motor or small-, medium- or high-speed gas engine. One of the best of these is the heavier torque arm unit, which consists of a small electric motor and single reduction gear mounted together on a spring-loaded torque arm which absorbs jerky motion and snatching, with a chain drive from the single reduction gear to the crankshaft operating the pitman, which crankshaft also serves as the fulcrum for the torque arm. Such a unit is rated at 25 H.P., and to give an idea of its performance in one typical well where a study was made, the following details are set down :

The pump was a 2-in. tubing liner type with plunger dia. 1¾ in. at 1729 metres, and actuated by a combined ⅞-in. and ¾-in. rod string. The stroke was 1·25 metres and strokes/metre 12. Production was 14 tons per day, maximum polish-rod load by dynamometer 6850 kg. Counterbalance was 5000 kg. An 18-kw. electric motor was employed, and the polish-rod H.P. was 5. The same well after adjustment of stroke is now producing 24 tons from the same depth, but load details have not yet been measured.

Probably the most popular unit is the double reduction-gear type, the double step-down in speed being needed because it is not possible to obtain the necessary reduction from prime mover speed to crank speed in one step. The total speed reduction is in the neighbourhood of 10 to 1, and where a high-speed motor is used, the further necessary reduction is obtained by the arrangement of the primary pulley sizes, usually a Vee-belt drive. The beam is mounted on the same base as the gear and motor or, if necessary, can be mounted on a separate foundation. The pitman can be single or double, depending on the loads handled and how the counterweighting is to be arranged, either on the beam end, the pitman or crank. The maximum standard stroke obtainable with these outfits is 1·82 metres (72 in.). The heaviest of these units will handle a polish-rod load of about 13 tons.

As time has progressed, wells have become steadily deeper, and with low crude prices, gaslift operation of small producers at big depths has become

uneconomical, so the long-stroke pumping unit has been successfully developed, and is now coming into general use where conditions demand. The unit is a modification of the standard beam and double reduction gear unit, but with the pitman drive to the beam so arranged as to function closer to the beam centre than was the case with the usual unit, thus giving a long stroke at the beam end. To meet the conditions of heavy load, the unit is fitted with a double crank, from which two pitmans transmit power to the beam. Straight-line motion at the beam end is in one case by a horsehead of effective length equal to the maximum possible stroke, and in another case by an arrangement of beam supports which give the beam hanger both vertical and horizontal movement, the resultant movement being a straight line. These long-stroke units have a maximum stroke of 336 cm. (132 in.), and can handle polish-rod loads up to about 14 tons at 20 strokes per minute.

Estimation of Available Fluid to be Pumped.

To pass from the surface installation to the type and size pump required, an estimate must be made of the liquid volume which is to be lifted and the level from which it is to be lifted. Since maximum liquid is available when all back pressure has been removed from the sand, one method is to bail with the largest-size bailer and as fast as possible, in order to fix the fluid level and the quantity recoverable with the fluid at that level. Since bailing at depth is necessarily slow, and size of bailer limited to the liner or oilstring diameter, the quantity recovered must often be considerably smaller than the real potential. Another method which gives the absolute maximum recoverable is to flow the well by gaslifting at different rates, controllable by varying beam sizes, and for each rate take a reading of the bottom-hole pressure. A curve can then be plotted showing drop in bottom-hole pressure against rate of flow. This curve will be a straight line for wells with small quantities of gas or with constant G/O ratio for varying rates, and if prolonged to cut the co-ordinate corresponding to static bottom-hole pressure will indicate the maximum rate of production for zero pressure at the sand-face. This is the quantity of production which, at least theoretically, is available for pumping, and can be used as a basis for calculating size of pump needed.

Pumps.

Types of pumps are many, but those usually employed are the tubing liner and the rod liner. These types are too well known to need any special description, but one or two points in connection with them are worth mentioning.

The essential difference between the types is, of course, that, in order to recondition the tubing liner pump it is necessary to pull the tubing string, while the complete rod-liner pump can be pulled on the rods. Consequently, in deep wells, other things being equal, there are big pulling operation economies to be made by using the rod-liner pump. Here it should be noted that without question it pays to buy the best quality pump and spares obtainable. Groove seal plungers give good service without

slippage, irrespective of depth, and it is found that cups are only necessary in odd cases of wells producing big percentages of water. The groove seal obtains its sealing effect by the swirling action of the liquid in the grooves, and it is possible that the viscosity of water being less than that of oil prevents this action being effective. It is also claimed that odd particles of sand are trapped in the grooves, thus preventing the scoring of liners.

Tubing Liner Pump.

The tubing liner pump is made in nominal sizes between 1 in. and 4 in., with the plunger diameter always $\frac{1}{4}$ in. smaller than the nominal size. Where pumps are set below 1000 metres, the practical sizes which can be conveniently used are the 2$\frac{1}{4}$-in. and the 2-in. nominal. Standard lengths of pump range from 5 ft. to 11 ft., with 2 ft. increments, and there are two standard plunger lengths—48 in. and 60 in. It has been found that the 48-in. plunger length gives satisfactory service with no measurable slippage. The plunger is set as close to the standing valve as possible to avoid gaslock, and the travelling valve is attached to the bottom of the plunger. For gassy conditions the Perry plunger is good, as it leaves the minimum clearance.

Rod-Liner Pump.

The rod-liner pump is made in nominal sizes of 2 in., 2$\frac{1}{2}$ in. and 3 in., but here again, for deep well pumping, the practical plunger sizes are $1\frac{1}{16}$ in. and 1$\frac{1}{4}$ in. for the 2-in. nominal size, and 1$\frac{3}{4}$ in. for the 2$\frac{1}{2}$-in. nominal size. Standard pump lengths are 9 ft., 10 ft., 12 ft. and 15 ft., and 48-in. plungers are usually satisfactory.

There are now manufactured four sizes of rods—$\frac{5}{8}$ in., $\frac{3}{4}$ in. $\frac{7}{8}$ in. and 1 in. —the latter being a comparatively new development.

Regarding the choice of sizes of tubing to be run with any particular rod string and pump, the tubing must be at least as big as the nominal size of the pump. Another consideration is the size of the rods, and it is not good practice to run $\frac{3}{4}$-in. rods inside tubing of less than 2-in. and $\frac{7}{8}$-in. rods inside tubing of less than 2$\frac{1}{2}$ in. Other than these minimum sizes there seems to be nothing against running larger sizes of tubing if so desired.

In the States one hears of the pump being set in a tubing anchor with packer at the appropriate level, and the rods work inside the casing. Where size of casing is large there would be danger of spoiling the rod string in case of a break, and possible difficulty in the efficient sealing of the packer. A tapered string of rods is indicated for all deep wells. The upper part of the string naturally has to carry a heavier load than the lower part, thus there is no point in increasing the load in the upper part by the use of over-sectioned rods at depth.

Where the well has already been on the pump, and dynamometer cards have been taken, the maximum load can be read and the rod string designed accordingly. The ideal rod string for any given conditions should be a true taper from top to bottom, since only then will the stress be constant over its whole length. Since in practice such a design is not practical, a combination of two rod sizes is usually run.

The amount of fluid which can be lifted per unit of time is a function of plunger size, effective plunger stroke and strokes per time unit. In any

pumping cycle the load is taken by the plunger on the up stroke and by the tubing on the down stroke, thus, as the polish-rod starts its upward travel, the plunger starts to rise more slowly, due to rod stretch as they take the load. At the same time the standing valve also starts to move upward, due to the tubing being relieved of load, and the standing valve follows the plunger until the plunger has taken over the whole load from the tubing. At the top of the polish-rod stroke the process is reversed. It will be seen that there is considerable loss of effective stroke of the plunger in the pump barrel, and this amounts to the sum of the respective tubing and rod stretch under the load considered. Thus the effective stroke is the polish-rod stroke minus the sum of the stretch of tubing and rods.

Plunger Sizes.

Pumping equipment manufacturers supply tables indicating loss of stroke in various combinations of rod and tubing sizes for different diameter pumps at varying depths, and since the polish-rod stroke is limited according to the available equipment, the effective plunger stroke can be worked out for these combinations. In a deep well there is then a limit to the plunger size which can be used at a given depth in combination with available rod strings, *i.e.* when the combined rod and tubing stretch or loss of stroke becomes equal to the polish-rod stroke. Thus the volume pumped at any depth is limited by these maximum plunger sizes.

Up to a certain point production per stroke can be increased by reducing plunger diameter, and therefore decreasing the load on rods; hence increasing effective plunger stroke, *i.e.* the gain in volume due to longer stroke, is greater than the loss in volume due to the decrease in plunger diameter. Beyond that point production will be less, since the gain in volume due to longer stroke will be less than the loss in volume due to smaller plunger.

It is possible to prove mathematically that maximum production per stroke is obtained with a plunger diameter that will produce a stretch equal to half the polish-rod stroke.

Again, referring to manufacturers' tables, the size of plunger for maximum production at any given depth can be chosen. At high speeds the effective plunger travel may be higher than that shown in any tables, owing to the whip in the rods due to their inertia.

Once the best plunger size is chosen, the only other variables are speed and stroke. Where available production does not require both maximum speed and stroke, it is best to use long stroke and slow speed to reduce friction losses, wear and vibration of equipment, fatigue of rod string and pump wear, besides saving in horse power, which is especially important in electrically-driven installations. An interesting set of figures published by a manufacturing firm shows that for a given quantity of fluid pumped the power required at 23 strokes per minute is four times that required for the same volume pumped at 2½ strokes per minute.

Loads and Dynamic Loads.

Considering the rods, the total load on upstroke carried by the rods is the sum of the weight of rods less weight of fluid displaced by rods, weight

of liquid carried by the effective plunger area, load caused by friction of fluid, plunger, rods and stuffing-box, dynamic load of rods and fluid due to acceleration. Of these the weight of rods, weight of fluid and dynamic load are the most important. It would be expected that the dynamic load would be highest at the beginning of the upstroke on the polish-rod, but in practice this is not so, due to the lag in plunger movement in respect of polish-rod movement, and also to the fact that the load is not transferred from tubing to rods and vice versa at the ends of the stroke, due to stretch.

Actually, the maximum load is usually found at about the middle of the polish-rod upstroke. The dynamic-load correction is usually expressed as a multiplication factor applied to the live load, and its magnitude depends on rod and fluid acceleration, and consequently on pumping speed. The factor can vary from 1·0 to about 1·5, and here again, where previous dynamometer cards are not available, manufacturers' charts give a good idea of what these loads can amount to under given conditions. The total load being known, the rod string can be checked, having in mind the allowable stress in the rod material used.

The power required to lift the fluid is the average power at the polish rod, minus counterbalance, plus losses in the pumping rig itself. Since the polish-rod load varies considerably during any one stroke, power must be available for dealing with the maximum load. Where an electric motor drive is being used through a reduction gear unit, it is most important for the counterbalancing to be as nearly exact as possible. However accurate the counterbalancing may be, there are still the irregularities in load during the stroke, and some of these may be taken care of by the energy stored in the rotating parts, particularly in the flywheel usually fitted to the high-speed shaft of the reduction gear. Thus the motor must be able to take care of these load fluctuations plus losses in the reduction gear unit, which usually has an efficiency of 60–70 per cent. The approximate horse power required to deal with the particular conditions of load, speed and stroke can be taken from tables, and the requisite size motor mounted; then, when the well is pumping, the power is checked by metering and the motor changed if necessary. In the band-wheel belt-drive type unit provided with facilities for hoisting and driven by gas engine, the efficiency of the rig is estimated at 35 per cent. and the power consumption is not so important, since as a rule fuel is cheap, but it is still of importance to arrange correct counterbalancing in order to prevent snatching and vibration of rig with eventual belt troubles. No system of counterbalancing can be perfect, since it is not possible to allow for peaks in polish-rod load; possibly the best system is to apply the counterweights on an extension of the back of the beam. The usual approximation used for the first counterbalancing of any well is to balance the weight of the rods plus half the fluid weight on the plunger. A better balance can afterwards be obtained by a study of dynamometer cards, or, where electric power is used, by a study of the peak power loads. The author has referred in several instances to manufacturers' reference tables. It must be understood that such are the extremely variable effects of friction, inertia and so forth that figures given in such tables vary considerably, and the final adjustment of the complete pumping installation can only be made by trial and error.

To consider some items not yet mentioned. When the hole is known to be crooked, hardened and ground couplings should be used as these cause the minimum wear on tubing walls, and consequent reduction in tubing pulling jobs due to leaks.

Also, for use in holes where the plunger stroke may not be exactly in line with the barrel, due to crookedness, a polished and hardened spiral guide can be used immediately above the plunger coupling, and save side wear on the pump liners.

Tubing Anchor.

Any deep well should have its tubing string safeguarded with a tubing anchor, and if possible a tubing catcher in addition set higher up on the string. The consequences of a dropped string of tubing are well known, and the anchor helps in two ways : first it is an insurance against accidents due to tubing wear, especially in crooked holes, and secondly it increases the effective plunger stroke by checking tubing stretch which in a 2000-meter well can be anything up to 15 in. The usual practice is to run the anchor one joint above the pump. Care should be taken that the holding area of the slips is as large as possible, to prevent casing deformation.

An important point regarding the setting of tubing anchors is to leave correct tension in the tubing string. If too much weight is on the anchor the tubing will flex, and the couplings will soon wear through the tubing walls. A recommended plan is to use a straight-pull dynamometer when setting the anchor, and as soon as the dynamometer shows that the slips are biting into the casing walls, to set the tubing at that point.

A similar dynamometer with lighter spring is also useful for setting the plunger and rods, since measurements at great depths are not always as accurate as they might be.

Gas Anchor.

The gas anchor is an important piece of equipment, essential to use in the pumping of gassy wells, and its design allows considerable scope for original thought. It functions first as an oil-gas separator, and secondly as a sand trap. In principle it consists of one or more joints of pipe so arranged as to extend above and below the pump, closed at its lower end, and provided with holes or slits near the top through which oil and gas enter. After entering the anchor the oil and gas separate, the gas passes upwards into the annular space between tubing and casing and escapes through the holes provided, and the dead oil downward towards the bottom of the gas anchor, from where it is sucked through a small-diameter pipe attached to the pump below the standing valve, sometimes called a " mosquito pipe." The gas anchor can be extended downwards by adding as many joints of pipe as desired, these serving as a sand-collecting trap which can be cleaned out whenever the pump is pulled. Some operators favour an extremely long gas anchor having the top extending to a point above the supposed liquid level of the well, some use a standard length for all wells, and others use as many concentric tubes as possible within the limits of the greatest possible diameter of outer tube which can be run into the particular well in question. The author would say that the

essentials are as follows: First, the gas anchor proper should consist of a single joint of pipe of 8–10 metres length of the greatest possible diameter that will fit into the well casing. This in order that the downward velocity of the oil will be as small as possible, giving the gas time to separate. Secondly, the entrance holes or slits should be within 1 metre of the top of the joint and 1 metre above the standing valve. Thirdly, the mosquito pipe need not be more than 2 metres long; this will leave 4–5 metres free to act as a sand-trap, but if any particular well has sandy conditions, more joints can be added to meet the special case.

Polish-Rod Fitments.

One or two points about the polish-rod fitments are worth mentioning. The polish-rod should be provided with a sturdy bolted clamp so fixed on the rod that it just clears the stuffing-box when the beam is at the bottom of the stroke; this will take the weight of the rods in case of accident to the outside installation, and prevent it falling on the pump, thus causing a possible parted string of tubing. Some reduction in sucker-rod fatigue can be accomplished by floating their weight on rubber cushions. This can be done by threading a circular block of rubber, together with an upper and lower retaining plate over the polish-rod, which assembly is arranged between the polish-rod clamp and the carrier bar of the beam hanger. The retaining plates are recessed so as to prevent spreading of the rubber block under load, and the holes through the plates, block and carrier bar must be large enough to allow free passage of the polish-rod. The resiliency of the rubber slightly retards the acceleration and deceleration of the rods at the stroke ends, and consequently smooths out the peak loads. According to dynamometer tests the reduction in peak load can be 5–8 per cent.

Paraffin Deposits.

In this country most deep wells are troubled with paraffin deposits to a greater or lesser degree. The usual deposit forms on the top 300–400 metres of tubing, and forms more quickly in gassy wells, due to the cooling effect of the gas as it expands on nearing the surface.

One method of reducing the trouble is the use of solvents introduced into the casing by means of some form of lubricator; such solvents have to be imported, and considerable quantities are needed. Waste also occurs, since the tubing, when eventually pulled, is often found to be covered on the outside from top to bottom with a thick coating of the liquid used, which in quantity can be considerable. The use of cups, made in two pieces and bolted together between the upset ends of a sucker rod and spaced 50–60 metres apart over the top 300–400 metres of rod string, has been tried, with the idea of pulling the top part of the rod string at appropriate intervals, thus removing paraffin deposit. The experiment was not very successful, as it was found that the cups tended to deform and break up, small pieces falling down and jamming the pump. The top 300–400 metres of rods can be fitted with hardened and ground spiral guide couplings, which clean out the deposits if pulled at suitable intervals. The use of steam injected into a jacket of concentric tubing extending down to the limit of

paraffin deposit is a solution, but steam is not always available, and boiler upkeep is costly. Another solution is to pull the top joints of tubing at intervals and replace them with clean joints kept ready, made up in stands in the derrick. Where numbers of wells are to be dealt with by this method, it means that quantities of tubing are kept idle, and there is also the risk of dropping the string. It is likely that the best all-round method is to make periodical injections of hot oil into the tubing after lifting the plunger and standing-valve. It is found that the quantity needed for efficient washing varies at different wells, but if sufficient is pumped to fill the tubing string, it will probably meet the case.

No pump is required, since the oil can be run in from a small lease tank so arranged as to have fall to the well mouth, and in the case of a group of wells a central tank can be arranged to serve the group. The temperature of injected oil is about 100° C. After the injection is finished, the standing valve is lowered into place and pumping resumed. The whole operation takes 2–4 hours.

The handling of salt water produced with the crude seems to present no great difficulty. Corrosion problems of the magnitude met with in other countries do not occur, and the author has come across only one case where rod string collars became so badly pitted that special alloy collars had to be provided. Alloy steel collars were made in the country and fitted, since when no further trouble has been experienced.

Emulsions are sometimes formed during the passage of the oil and water mixture through the pump, especially if the gas anchor is not efficient, or if the pump is worn. The changing over from gaslift to pump on a wet well is often accompanied by big reductions in the cost of emulsion treatment; the salt water also is effective in keeping the tubing free from paraffin deposits.

Deep wells with high fluid levels and high percentages of water can sometimes be handled economically by pumping with a large-bore pump from some point high up in the casing. This procedure is also likely to help combat the approaching water, since it keeps a steady back pressure in the formation. One such well about 1800 metres deep was producing 40 tons of water with 4 tons of oil with tubing set near perforations and at a big injected gas expense. On being turned over to the pump it produces 38 tons of water and 4 tons of oil from a pumping depth of 450 metres, using a 2½ in. tubing liner pump and ⅞ in. rods. Incidentally the cost of cleaning the crude was extremely high on gaslift, since the emulsion was very tight, and had to be treated by heat and chemicals. On the pump no emulsion is produced, and the water settles out in the lease tanks.

Economies in Pumping Lease Operations.

In connection with pumping lease operations, attention paid to certain points will result in big savings. A pump servicing workshop may be provided with mandrils for the assembly of pump liners. These mandrils are $\frac{1}{1000}$ inch (— 1) smaller than the standard liner size. Two sizes of plunger can be carried in stock for the 1¼-in. and smaller diameter pumps (that is, — 3 and — 1) and three sizes (— 5, — 3, and — 1) for the larger diameter pumps. The servicing shop sees that the pumps are sent out fitted with the correct-

size plungers according to liner wear, and that other worn parts are replaced. It is now possible to purchase oversize plungers + 20 and + 40, so that worn liners can be twice re-bored.

Other points which merit attention are :

The selection and training of pulling gangs, who should be educated in the rudiments of pumping, and the use and care of tools. A gang should never be split up, and each individual should have his special job in a pulling operation.

The provision of suitable tools and their arrangement on the derrick floor. The care of these tools can be centralized in a tool store, where they will be checked at regular intervals. A lubrication programme, especially where complicated rod liners exist, since such items as pendulums, swings, etc., can be easily neglected.

Possibilities of pumping lease production to the tank farm from a pump running off the back crank of a well or off central power.

Possibility of supplying the lease with water from a local source using a similar pump.

The use of low-pressure heaters where high-pressure steam for power is not required.

The importance of standardizing beams, pitmans, countershafts and a multitude of other accessories.

The care of sucker rods against thread damage and bending.

The keeping of adequate records, regarding pumping conditions and performance of the various items of equipment together with shut down time and causes of such.

Although many of the individual economies which are made are small, their total may amount to some figure which will be the deciding factor whether or not pumping can be continued profitably at a well, or whether it should be abandoned.

The author has tried in this paper to touch on the important points in connection with the practice of deep-well pumping, especially relating to this country. He has found, however, that it is difficult to convey in a few words a clear picture of certain aspects of the subject. In conclusion, the point he would bring out is that, given suitable equipment, there appears to be no reason why the deepest wells at present producing in this country should not eventually be pumped.

THE APPLICATION OF AUTOMATIC CONTROL TO REFINERY PROCESS OPERATIONS.*

By S. W. Adey, B.Sc., A.R.C.S., F.I.C. (Associate Member).

Synopsis.

The paper opens with a brief description of the more important types of process control instruments and their underlying theory. The selection of methods of control and the installation of instruments are next discussed and the importance of close co-operation between plant operator, designer and instrument manufacturer is emphasized.

Stabilizing and Automatic Re-Set Devices, and their significance in the control of continuous processes, are explained.

Finally the economic aspects of the subject are reviewed, emphasis being laid upon the fact that while some instruments definitely improve operating efficiency and quality of product, others serve purely as labour-saving devices. The paper concludes with a note on the organization of instrument repair services.

Introduction.

Most petroleum refinery processes are nowadays carried out continuously, and the work of operation consists largely in holding at a predetermined value certain physical conditions of pressure, temperature, flow rate and liquid level. These physical conditions then serve to ensure the proper functioning of the plant, whether the process itself be physical or chemical, so that products of constant quality are obtained.

Automatic control may be applied to certain batch operations, but the field is wider if the process is continuous, so that modern, continuous plant has fostered the demand for such devices. Instrumentation is, therefore, comparatively new, and only in the last ten or twelve years has it been able to show any real saving in labour. For such a saving to be achieved it is necessary for the work of instrument maintenance to be reduced to a reasonable figure, and also for the instruments themselves to be thoroughly reliable. There must be no need for " stand-by " operating labour in case of failure.

Labour-saving is not, however, the sole purpose of automatic control. Manual control of certain operating conditions, *e.g.* cracking still pressure, cannot be made as effective as automatic control, so that solely on the grounds of operating efficiency and constant quality of product, there may be a case for dispensing with the human element. This part of the subject will be dealt with more fully later on.

In the design and installation of control instruments it is very easy to be ingenious, but much more difficult to be practical. Such equipment is at present passing through very much the same stage as did the accessories on motor-cars a few years ago, by which it is meant that even to-day a piece of refinery plant may be designed and built, and then the instruments added as an afterthought. Until instruments come to be considered as much an integral part of the plant as, say, the pumps, they will justify as much criticism as did the motor-car accessories of old.

* Paper presented for Discussion at the One Hundred and Seventy-ninth General Meeting of the Institution of Petroleum Technologists held on January 11th, 1938.

It is only during the last four or five years that instrument-makers have obtained a real grasp of the processes for which they were trying to build control gear, and the value of what knowledge they have gained is already showing up in more efficient and more reliable equipment. It must be realized that the control of any given physical condition, such as temperature, is a different problem on every kind of plant, and no one fixed type of instrument can possibly meet every requirement efficiently.

The first and second parts of this paper cover a description of the basic types of control instrument used in petroleum refineries and their application to specific problems. It is not intended, neither is it possible, to describe all the better-known makes and types, and where particular ones are mentioned, this is purely by way of illustration.

The third part of the paper deals with the economic aspect of applying automatic control, and is intended mainly for those who require guidance in deciding, as a matter of policy, whether automatic control should be adopted or not. This subject has been dealt with last, not because it is considered less important, but because some understanding of the technical aspect is a help in reaching a decision.

I. Theory and Basic Types of Instrument.

All instruments consist essentially of two parts: first that which measures the physical condition to be controlled, and secondly that which does the controlling. The second element is often so attractively ingenious that one is apt to ignore the first, wherein most of the difficulties of the problem may reside, because it is there that the closest co-operation between instrument-maker and plant-designer is required. For this reason, each basic type of instrument will be considered as consisting of the above two separate items.

(i) *Gas-Pressure Controllers.*

These are used for maintaining a constant pressure in natural gas plants, stabilizer columns, cracking still columns, etc. The earliest type consisted of a double beat-valve held in the open or closed position by means of a weight and lever, and actuated by means of a diaphragm upon which the gas pressed. In so far as a simple weight and lever is a very poor pressure-measuring device, just so far was this type of controller inadequate.

A spring was soon substituted for the weight and lever and, even to-day, where close control is not required this type is still seen. So simple a mechanical contrivance, however, lacks sensitivity, because the force required to overcome mechanical friction is too large in comparison with that resulting from a small change in gas pressure on the diaphragm. Just as with motor-car brakes, some form of servo motor or its equivalent is necessary.

To illustrate some of the important advances which have taken place in the last few years, a modern type of gas-pressure controller is shown in Fig. 1, the main features of which are as follows:—

(*a*) The main controlling valve is actuated by air, which is supplied to the instrument at a constant pressure, usually 25 lb. per sq. inch. The gas pressure to be controlled is admitted to a small diaphragm, to which is

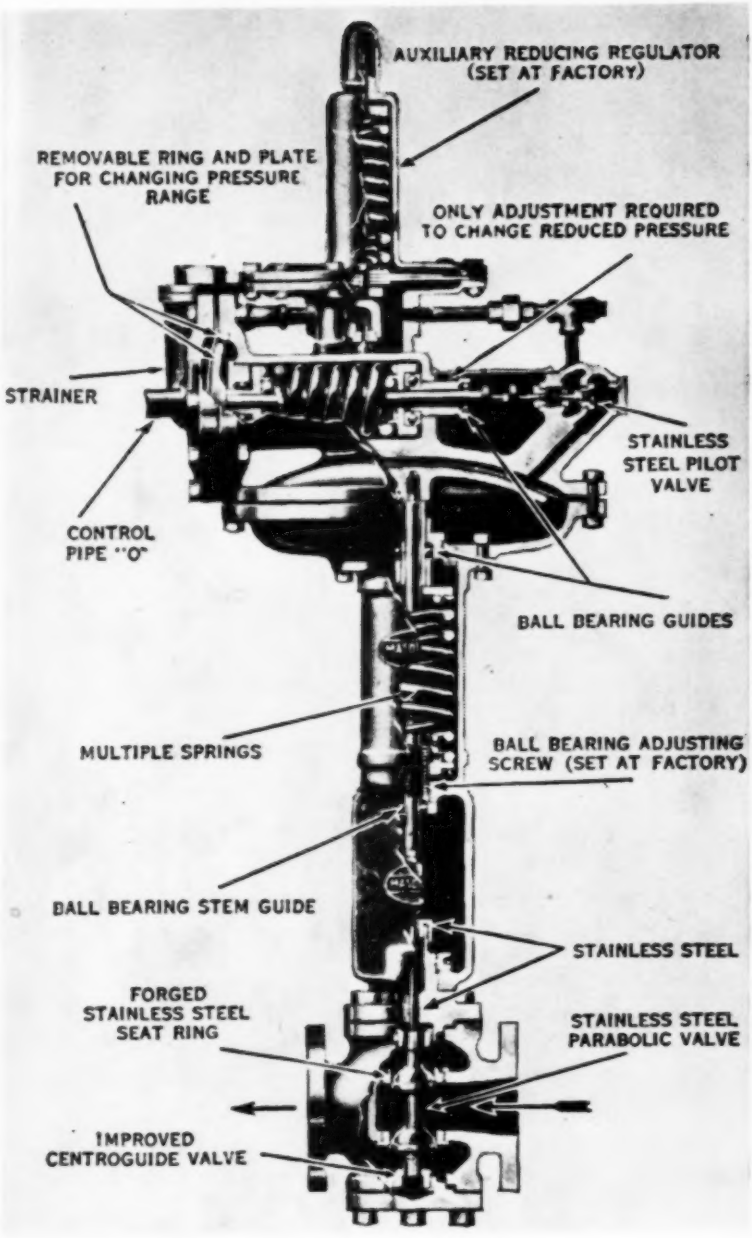

FIG. 1.

MODERN TYPE OF GAS-PRESSURE REGULATOR.

(By permission of The Crosby Valve & Engineering Co., Ltd.)

To face p. 126.

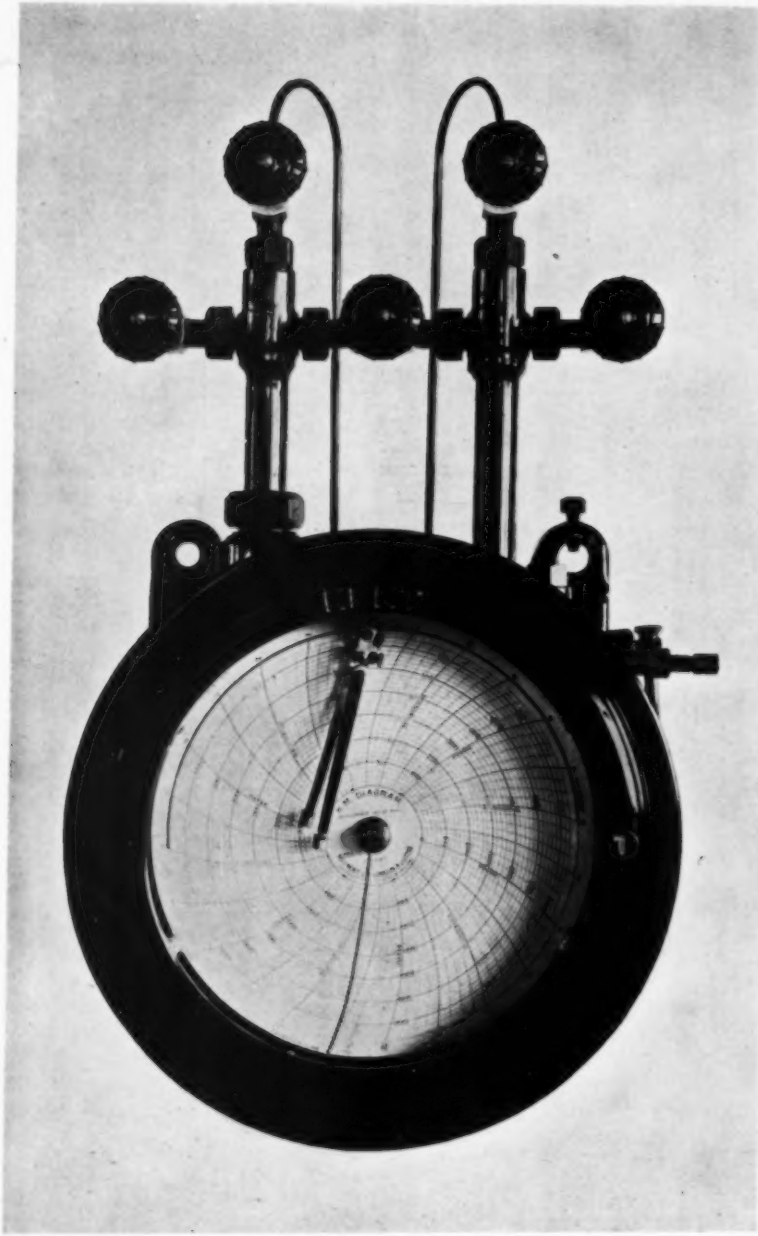

FIG. 3.

ORIFICE METER FOR OILS OR GAS.

(By permission of Messrs. George Kent, Ltd.)

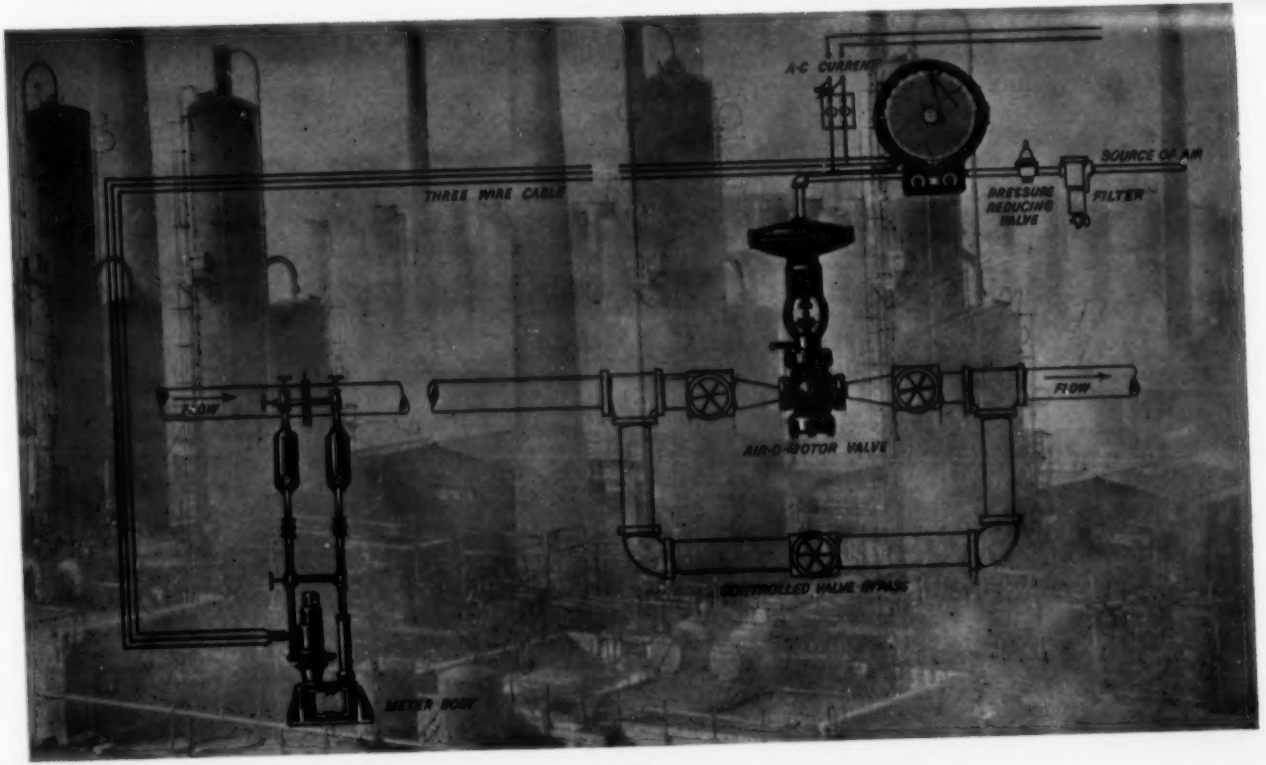

Fig. 4.
FLOW CONTROLLER WITH ELECTRICALLY OPERATED DISTANCE RECORDER.
(By permission of Messrs. Honeywell-Brown, Ltd.)

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attached an air valve, more or less air being thereby admitted to the main diaphragm as the gas pressure changes. The rate at which air is admitted from the constant-pressure supply to the main diaphragm depends on the gas pressure, but since there is also a steady leak-off to atmosphere from above the main diaphragm, the pressure on it will not change unless the rate of supply differs from the rate of leak-off. Now, the physical dimensions of the gas-actuated air-valve are fixed, whilst the leak-off is manually adjustable, so that the sensitivity of the instrument can be varied by changing the rate of leak-off. Thus the separation of the measuring device, *i.e.* the smaller gas-actuated diaphragm and spring, from the controlling device which is the main valve and diaphragm enables the characteristics of the instrument to be varied somewhat to meet individual conditions. For example, a vessel the pressure of which it is required to control may be receiving gas in small bursts; either the pressure may be held quite constant by adjusting the controller to eliminate the gas in corresponding small bursts, or else the pressure in the vessel may be allowed to vary between narrow limits and the gas let off at a fairly steady rate. If it is desired to meter the outgoing gas on a recording meter and obtain a readable flow-chart, the latter will be preferable. In the particular case cited above, where the gas supply to the vessel is fluctuating rapidly, it is important to bear in mind that no controller could maintain a perfectly steady pressure and at the same time a meterable outflow; this point is often lost sight of by operators who expect what is, in effect, a physical impossibility unless the vessel is very large in comparison with the fluctuating input. The ability to provide an easily meterable flow rate is still further enhanced by employing stabilizing and damping devices, to be described later.

(*b*) To reduce friction, all important moving parts are on grease-packed ball-bearings, and the main spindle passing through the stuffing-box is very thin.

(*c*) The seats of the main double-beat valve are parabolic in shape, and not merely the conventional bevelled mushroom type. This gives much better flow control at small openings. Other devices, such as the V-ported cylinder, are equally effective.

(*d*) The rubberized diaphragm on which the gas presses is covered with a layer of oiled silk to resist the effect of hydrocarbon gas, but even so it may be advisable to interpose a liquid seal between this diaphragm and the gas, further to reduce the risk of the latter being rotted away.

(ii) *Liquid-Level Controllers.*

As with the pressure controllers described above, the controlling item is a spring-loaded diaphragm valve of the balanced, double-beat type, air being the operating medium. Valves directly controlled from a float through a mechanical linkage are not usually so satisfactory, and suffer the further disadvantage that the control valve must be placed close to the vessel in which the liquid level is to be held steady.

Particularly in the case of liquid-level controllers is the level measuring unit of prime importance. Two types are in common use: the ball float and the mercury manometer. The ball-float variety takes two forms: either with the float in a separate small vessel termed the "kidney" or

with the float right inside the main receiver or column base. Floats are liable to puncture or be crushed when the vessel is being pressure-tested, so that the latter type should not be used unless occasion demands, *e.g.* when controlling thick tar. Where a "kidney" is used, this is connected

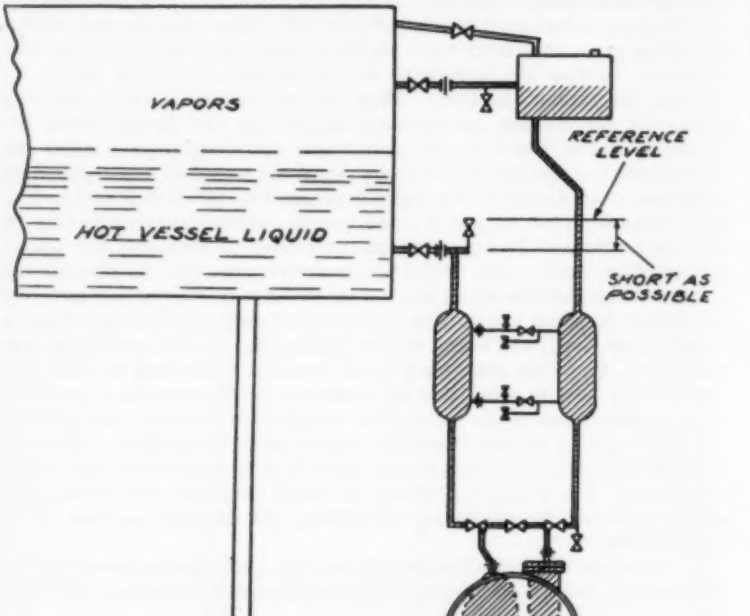

FIG. 2.

MANOMETER TYPE LIQUID-LEVEL CONTROLLER.

(By permission of Messrs. Foxboro-Yoxall, Ltd.)

to the main vessel by two 2-in. lines fitted with block valves to enable the float to be isolated and changed if necessary. By this means also any swirl in the main vessel is rendered less likely to affect the position taken up by the float. The float arm rotates a spindle which passes through a gland in

the "kidney." The partial rotation of this spindle is made to control the supply of air from a constant-pressure source to the diaphragm of the control valve, and so regulate the level. If the liquid being controlled is under pressure, it is possible that the float spindle will be subjected to end thrust on that account, and unless there is an effective ball-thrust race to take this up, excessive friction will result, to the detriment of proper working of the instrument.

The second type of liquid-level measuring device is the mercury manometer in the same form as used in orifice meters. In this case one arm of the manometer is connected below the liquid level and one above, so that the meter pen arm records the change in liquid head. The pen arm or its equivalent then operates an air relay in a similar manner to the float spindle in the first type. An instrument working on this principle is shown in Fig. 2. If liquid is entering a vessel in short bursts, it is quite impossible for a level controller on the outlet to maintain both a steady level and a steady, meterable outflow; one or the other must be allowed to vary. The manometer type of level controller is very suitable for dealing with such cases, as it can be designed to allow the level to swing quite a lot while it maintains a reasonably steady flow, and so permit metering of the liquid stream. Generally speaking, it is not quite so suitable for the control of heavy, hot-tar levels as the internal-float type.

(iii) *Flow Meters and Flow Controllers.*

By far the most popular type of flow meter is the orifice meter, an example of which is shown in Fig. 3. In this instrument the difference in hydrostatic head put up by an orifice inserted in the fluid stream is impressed on a mercury manometer, which, *via* a steel float, operates a pen arm on a circular chart. Where gas under pressure is being metered, a second pen arm records the static pressure simultaneously on the same chart.

It is not the purpose of this paper to discuss metering in detail, as this is a very wide subject, but one or two points may be mentioned. The commercial types of orifice meter should not be expected to measure pulsating flow with accuracy, hence steps should be taken in the design of the plant to see that flows do not pulsate. The second point is that, in the cases of hydrocarbon gases under pressure, allowance must be made for the deviation from Boyle's Law where calculation shows this to be necessary. Thirdly, orifice meters will not give accurate results where the flow is in the viscous region unless special corrections are applied. In practice it pays to avoid such conditions, because the correction factors are seriously influenced by temperature and quality of the liquid being metered.

There are on the market a number of displacement meters which can be used for viscous liquids, but the fact that they do not measure the instantaneous rate of flow is often a disadvantage from the operators' point of view.

The flow controller is an adaptation of the orifice meter in which the pen-arm mechanism is made to operate a diaphragm valve on the metered stream *via* an air relay. An example is shown in Fig. 4. In this case the mercury manometer operates an inductance bridge system, so that the differential pressure is transmitted to the recorder electrically. This recorder

then operates the air relay to the diaphragm-type flow-control valve, so that if the metered stream tends to change in flow rate, the control valve checks it.

(iv) *Temperature Controllers.*

Temperature controllers operate in a variety of ways, but the two commonest types, which cover most requirements, employ vapour-pressure bulbs and electrical pyrometers, respectively, as the measuring devices. In the latter case certain makes are entirely electric, in that the pyrometer is caused to relay one or more electric motors which operate valves on the heating-medium supply.

Those temperature controllers in which the temperature measurement is obtained by the change in vapour pressure of a liquid in a bulb invariably use air as the main controlling medium. The pressure in the heated bulb causes a bellows or Bourdon tube to expand or contract, and this in turn controls the air supply to a diaphragm valve on the fuel or steam supply. These instruments are quite suitable for temperatures within the range of the measuring device, but for higher temperatures, *e.g.* cracking still outlets, the pyrometer type is advisable.

A very modern example of the latter type, employing a potentiometer-type pyrometer actuating, in this case, an air relay is shown in Fig. 5. This instrument, which is typical of up-to-date air-relay practice, operates as follows :

The rotation of the slide-wire disc, which is a measure of the temperature, opens or closes a flapper valve on a restricted air supply to the diaphragm of the burner gas or steam-control valve, thus causing this valve to increase or decrease the supply of heating medium. To stabilize the system, *i.e.* to avoid hunting, there is a second control of air pressure to the valve diaphragm. This is effected by taking a pressure lead from the burner gas or steam main *after* the control valve, and causing this to operate the flapper valve on the air supply in the opposite direction to the slide-wire disc, but to a lesser extent. Some such device is essential in the case of, say, a pipe-still outlet temperature controller, where the time taken for a *reasonable* increment in burner gas flow to affect the temperature measured is considerable. Stabilizing devices are discussed generally in a separate paragraph, because in large continuous plant they are of supreme importance.

The above brief description of the four main types of controllers, pressure, level, flow and temperature suffices for the purpose of this paper.

II. Technical Considerations in the Application of Automatic Control.

This aspect of the subject will be considered under three headings—Selection of the Conditions to be Controlled, Selection of the Point of Control, Time Lag and the Stabilization of Controllers.

(i) *Selection of Conditions to be Controlled.*

In the first case, let us consider a crude-oil distillation unit. If a column is operating at constant pressure and receiving a constant-quality feed,

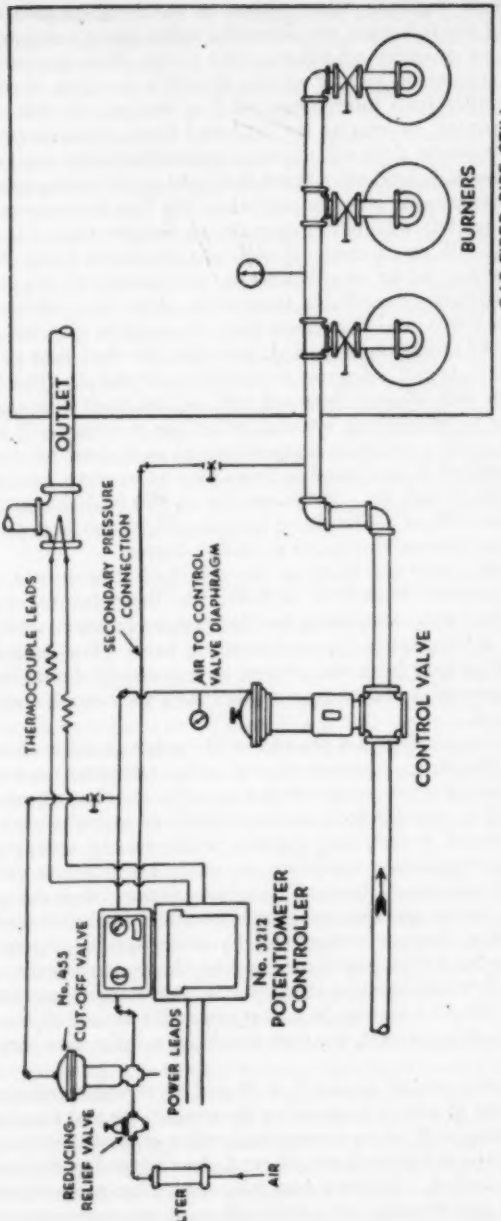

Fig. 5.

PYROMETER TYPE AIR OPERATED FURNACE TEMPERATURE CONTROLLER.

(By permission of The Crosby Valve and Engineering Co., Ltd.)

then the quality of distillate taken either as overhead or side streams will vary if any of the following are changed: reflux ratio, temperature at point of off-take or quantity off-taken. The reflux ratio determines the closeness of the separation and, if all the distillate is taken overhead, a reflux ratio controller (two interconnected flow controllers) will fix this. In these circumstances, so long as the feed and the feed temperature are constant, this instrument alone will ensure a constant-quality overhead and residue, more or less independent of the rate of feed up to the capacity of the column. If, however, side streams are taken off, this instrument is less effective, and we are left with either quantity or temperature as the useful control conditions. Where a crude of constant quality is being distilled, experience shows that, as far as side streams are concerned, quantity off-taken is a very satisfactory condition to control. Flow controllers may be located on the draw-offs, and once these have been set to give the quality required, no further attention is needed, provided the feed rate and temperature do not change and adequate top reflux is provided. The internal reflux below each side stream draw-off will adjust itself automatically. The alternative is to adjust this internal reflux (or the draw-off, which is the same thing) to give a constant temperature at each draw-off plate, but in practice this method is not found to be so easy to operate, whatever its theoretical advantage may be. If the quality of the feed should change, the flow controllers will, of course, have to be re-set, but so in practice will the temperature regulators, though to a smaller degree.

To sum up, such a unit will have, as the principal instruments, a pipe-still outlet temperature controller, a tower-top temperature controller operating the reflux, flow controllers for the various kerosene and gas-oil side streams and a level controller on the tower base. The same applies to a vacuum still making lube cuts, where it is generally found that the division between pressable and non-pressable cuts is very much a matter of percentage taken off.

The second case to consider is a pressure-still cracking residue to tar, gas-oil and pressure distillate. Control of coil outlet temperature to within 2° F. and gas separator pressure to within 1 per cent. are the first essentials. The former should be possible with modern stabilized instruments and gas firing, and the second is certainly possible under steady operating conditions. The only remaining conditions the control of which is debatable are feed to the coil and gas-oil draw-off from the column. It is the author's view that the flow to the cracking coil should invariably be controlled by an instrument, and any changes necessitated by levels building up or falling should be dealt with by the operator moving the control point of that instrument if the flow rate must be changed. If the charge pump is steam-driven, the most effective system is a flow controller acting on the steam supply; if electric drive is used, the flow controller must act on part of the oil stream itself.

With regard to the gas-oil draw-off, it should be remembered that, due to the large amount of excess heat fed to the evaporator and fractionating column of a cracking unit, there is usually a reflux point below the gas-oil draw-off by which the quantity of gas-oil (and also the quality of the recycle stock) may be controlled. Either a flow ratio controller, proportioning the reflux to the nett gas-oil make, or a draw-off point temperature controller

might be considered, but in practice the latter is better. The reason for this is purely an operating one. Cracking operations sometimes get out of hand, and a not uncommon trouble is for top reflux to be lost, in which case the gas-oil produced will momentarily decrease. If a ratio controller were used to fix the amount of intermediate reflux, this also would decrease, whereas, to get control of the unit again, an increase is required. A temperature controller would, in nearly all cases, help to give this.

A third case is the gasoline stabilizer, the proper function of which is to produce, as a bottom product, the maximum yield of gasoline of a given vapour pressure. The operating pressure being fixed, it is therefore essential to fix the temperature of the final product, leaving the column base or the reboiler, as the case may be, for which purpose a temperature controller is naturally selected. In order to ensure the maximum yield of stable gasoline, the degree of fractionation must be controlled both in the rectifying and stripping sections. Usually, the most satisfactory way of doing this is to employ a feed-plate temperature controller regulating the steam to the preheater and a reflux ratio controller proportioning the reflux to the nett overhead product, liquid or gas. To employ temperature controllers, both top and bottom may be quite unsound, because it represents an attempt to divide a feed having, in most cases, a varying vapour pressure into two components of fixed vapour pressures. Only in one case in a thousand would this be consistent with maximum yield.

(ii) *Selection of Point of Control.*

To one who is fully acquainted with the operation and duties of a plant, the selection of the point at which the measuring part of a controller should be attached is largely a matter of common sense, but too often the decision is left to someone without the necessary knowledge. The following observations may help to avoid mistakes in this important matter.

First of all it is necessary to decide what the instrument is really meant to control, and then to connect it up to measure the quantity which really matters, *e.g.* the bulb of a stabilizer column base temperature controller should not be put in the reboiler vapour outlet, but in the final hot liquid product just before it leaves the column.

In the case of a crude oil pipe-still the important temperature is the flashing temperature of the crude as it enters the column, not that at the end of the pipe-still itself, therefore the controller should be placed close to the column just before the release valve, if any. Every operator has experienced the minor upset to a plant which is caused by a sudden shower of rain cooling the line (lagged or not) from the still to the tower. The instrument can help to avoid that if it is properly installed.

The bulbs of column-head temperature controllers require especial care. They should be as close to the vapours rising from the top plate as is possible without risk of being splashed by liquid, but they must be kept well away from reflux. A safe place is in the vapour line, just where it leaves the column. Whatever may be desirable theoretically, the liquid and vapour on a plate or in a column base are never found to be at the same temperature, so that a temperature bulb must be wholly in one or the other.

The pressure tap for a pressure controller should be connected to a point

where flow is steady or the vapour is quiescent, not close to the controller itself. Where distillation is being carried out under pressure and vapours pass from a column through partial condensers to a gas separator vessel, it sometimes pays to take the pressure tap from the column itself instead of from the gas separator, because of surging in the condensers.

Where the temperature of a side stream draw-off has to be controlled, it is generally good policy to place the bulb in the vapours rising from the plate below the draw-off plate.

In all cases where temperature bulbs are inserted into columns they should enter at least 2 ft., or one-half of the column diameter, whichever is less.

When manometer-type level controllers are used to control the level of hot liquids, care must be taken to instal the vapour leg so that condensation of vapour cannot occur in it. Usually this means employing gas-oil seal pots.

In most cases, modern stabilized controllers operate most effectively where the whole of the fluid being controlled passes through the diaphragm valve. These valves should be placed on a partly open by-pass only if experience shows this to be necessary. Nevertheless, the designer should always provide a by-pass line for maintenance purposes, unless cost is prohibitive.

(iii) *Stabilization and Time Lag.*

In many cases there is an appreciable time lag in refinery processes, in the sense that from the moment when a controller attempts to correct an out-of-balance condition to the moment when the measuring instrument can record the correction effected, is a measurable length of time. The uncontrolled time lag in modern instruments themselves is negligible, and if they are installed in accordance with the observations made in the preceding section there will remain only the necessary process time lag itself to consider. The ill effects consequent upon this, however, would be enough to interfere seriously with the satisfactory working of most of the earlier types of instrument, and even to-day it makes automatic control much more difficult than it would be otherwise.

The relationship between process time lag and the instrument is extremely complex, but the important point to bear in mind is that when a condition change—say, a small change in pipe-still outlet temperature—occurs a controller can measure only the magnitude of the change itself, and not the magnitude of the force causing it.

From this it follows that the instrument cannot determine (nor could any human agency, except by experience) the exact amount of correction to apply; whence every control instrument must be designed basically to over-correct the condition change, if it is to control at all. Now, the longer the period of time between the controller coming into action, *i.e.* the moment when the over-correction is first applied and the moment when the measuring element can record this and cause the controller to commence under-correcting, the greater will be the amplitude of the swing set up. For example, in the case of the pipe-still many seconds may elapse before the effect of an excess of burner gas is felt at the oil outlet, *i.e.* before the controller can start to close the burner gas valve. Theoretically, there is

no reason why the resultant temperature swing should ever die down and, in practice, with instruments of a few years ago, it often did not.

In addition to the above, there is another factor, connected with the instrument itself, which, though fundamentally distinct, makes the above

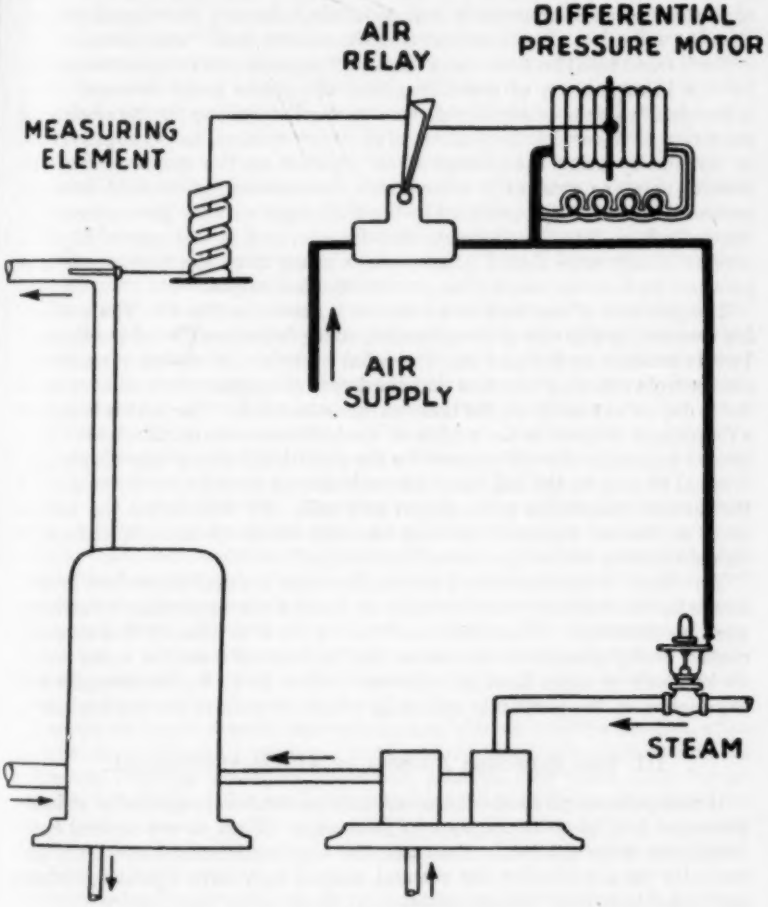

FIG. 6.

AUTOMATIC RE-SET APPLIED TO TEMPERATURE CONTROLLER.

(By permission of Messrs. Foxboro-Yoxall, Ltd.)

situation worse. Almost all instruments in their simplest form possess a definite relationship between the condition change recorded on the measuring element and the degree of opening of the control valve, *e.g.* if a controller is set to hold 600° F. on a pipe-still outlet when 50,000 cu. ft. per hour of

burner gas are passed, then, supposing more burner gas is required, the temperature will have to fall in order that the control valve may open. Hence, if there is a fluctuating rate of feed to the pipe-still, the controller cannot help but allow a fluctuating outlet temperature. This is why, a few years ago, operators were obliged to " re-set " their instruments every time there was an appreciable change in throughput. Here again process time lag will cause a continual swing in the " controlled " temperature.

Both these troubles have been largely eliminated in modern instruments by the incorporation of stabilizing and automatic re-set devices. The principle of these is briefly as follows : instead of waiting for the controlled condition to re-correct the position of the control valve, an attempt is made to do this by using the change in air pressure on the diaphragm of the control valve as soon as it occurs and also the change in fluid flow (or pressure) immediately controlled by the diaphragm valve. The instruments shown in Figs. 2 to 5 incorporate this feature, and in the case of Fig. 5 it will be clearly seen that a connection is taken from the burner gas line pressure back to the controlling part of the instrument.

The principle of one such re-set device is shown in Fig. 6. The measuring element, in this case a thermometer, controls the position of the flapper, but its relation to the seat can be varied by means of the air pressure on the control valve diaphragm so that the degree of opening of the control valve is not dependent solely on the temperature measured. The seat is linked to a diaphragm located in the middle of the bellows shown on the right. Following a change, the air pressure to the right-hand side of the diaphragm is equal to that on the left-hand side only after a period of time because of the air-flow restriction tube, shown as a coil. By this means the instrument is enabled to detect and use to some extent the rate of change of temperature as well as the actual change itself.

The effect of stabilizing and automatic re-set features in modern instruments has been almost revolutionary as far as their application to refinery work is concerned. These features have, for the first time, made automatic control really possible in the sense that instruments can, in many cases, do as much or more than an operator is able to do by forethought and experience, in the particular sphere in which controllers are applicable.

III. The Economic Aspects of Automatic Control.

It was pointed out in the Introduction that automatic control of refinery processes can be advantageous in two ways. First it can control some conditions more efficiently than can the most experienced operator, and secondly its substitution for manual control may save operating labour and possibly overall running costs.

It is wise policy for a Refinery Management to insist upon the use of instruments of the first class, *i.e.* those which, in the opinion of the senior operating staff, will result in better operating efficiency. An example is the automatic control of pressure on gas plants and cracking-plant columns. The installation of such instruments will result in an incidental saving of operating labour, but, together with meters necessary in any case, they imply the existence of an organization to effect their adjustment and repair. The question then comes, as to whether this organization shall be enlarged

to take care of instruments of the second class, *i.e.* those installed purely to save operating labour.

A fairly close study of actual refinery operating labour costs in the U.S.A., Europe and the Middle East leads the author to believe that, despite the large discrepancy in wages rates, there is not a very great difference in total wage bill per ton processed, because the cheaper labour is required in larger quantities. Real savings in labour costs are effected principally by employing large units and paying close attention to their layout and location with respect to other units. The most effective layout of a unit intended for hand control may often be improved upon from the mechanical aspect if automatic control is substituted, because the latter lends itself to distance operation. As examples of this, it is possible to locate pumps close to their individual duties, instead of grouping them in a single pump-house and employing long suction lines. Also furnace firing fronts may face away from the unit, with consequent increase in safety. Such points as these and the possible saving in capital cost accruing from them need to be taken into account, especially in large units.

The effect of automatic control on safety must always be considered, and it should not, at the present stage of development, be installed to such an extent as to reduce the labour available to deal with an emergency below a reasonable minimum. In this connection it must be borne in mind that automatic operation tends to reduce the familiarity of the plant attendants with the functioning of the unit. In an emergency, operators on a mechanically-controlled unit cannot be expected to act so quickly as if they had been controlling conditions themselves from day to day. The author has found first-class firemen on a cracking unit incapable of firing accurately by hand six months after automatic furnace temperature control had been installed. Against all this it must be conceded that centralized control in a single control house enables a really experienced operator to notice out-of-balance conditions more quickly, and renders him much more effective in an emergency unless the instruments themselves fail. A sound electrical supply and an auxiliary air system intelligently connected in render this latter contingency very remote, as experience has shown.

Certain electrical control instruments may themselves be a fire risk, even though they belong to classes of instruments commonly employed in oil refineries. Special attention should be paid to this point. As far as possible all gauge and instrument lines to the control boards should be fitted with water or gas-oil seals and, if proper attention is paid to this at the start, the risk of fire in a control-room can be reduced to negligible proportions.

If operating labour costs are to be saved by means of automatic controllers, centralization of the instruments and recorders is essential, which in turn means that to obtain the full benefit in savings, blow-down and similar valves should be capable of remote manual operation. The air-operated, hydraulic or electrical gear for this purpose is an added capital expenditure which must be taken into account.

From what has been said, it will be seen that the factors affecting a decision for or against automatic control will vary largely with circumstances, such as unit size, availability of highly skilled instrument maintenance

labour and number of units in the refinery. The maintenance cost per instrument will be lower where a large number are employed. It is clearly not possible to lay down hard-and-fast rules, but the following example may serve to give an idea of what is to be expected from the installation of automatic control on a large crude distillation unit :—

	£
Average cost of one instrument	100
Installation, including piping and by-pass valves	100
Total capital outlay, per instrument	200
Allowing 5 per cent. interest on capital outlay and ten years life, the cost of the instrument per annum becomes	30
Given a good service department in a large refinery the overall maintenance cost per annum would be approximately	5
Total cost per instrument per annum	35
Assuming that 25 such instruments were used, the total annual cost would be	875

The saving in operating labour, under favourable conditions, would be from two to three men per shift or six to nine men per 24-hour day. At £150 p.a. per man this represents a saving of from *£900 to £1350* in labour costs to be offset against *£875* for the controllers. In favour of the instruments, it may safely be said that operation would be smoother, and in the case of a really large unit, such as that in mind, an emergency could be handled more expeditiously. No allowance has been made for the installation of remote operated blow-down valves, but the capital cost of these should easily be saved by the simplified and improved unit layout rendered possible by the use of automatic control. For those who are contemplating the purchase of an automatically controlled unit for the first time, and who may therefore be a little dubious as to what is to be expected, it may be mentioned that many instruments can be purchased, to include hand as well as automatic distance operation. These enable the unit to be run manually from the control-room, even though the more complicated parts of the automatic gear are out of action. It is the author's experience that, in any case, operators frequently prefer to use this manual distance control when bringing a unit on stream.

There remains the question of instrument maintenance costs. The first essential here is to staff the repair shop only with thoroughly qualified men, who must understand the refinery process as well as their own job. Frequent changing of staff should be avoided. It is often found that after working for some years around the refinery, the more ambitious among them make first-class operators by virtue of the process knowledge which they have gained on instrument adjustment work.

In some refineries the operators themselves are encouraged to learn sufficient about the control gear to enable them to effect minor repairs on site, whilst in others this practice is discouraged. In a small refinery there may be some economy in allowing operators to work on instruments, and also this work serves to relieve the monotony of keeping watch on an automatically controlled unit. However, in a large works, employing many operators, this course is hardly practicable, because with the increasing complication of instruments it is bound to lead to damage being done by ignorance, which ignorance cannot always be tracked down and eradicated. In a 200,000-brl. refinery with which the author has been closely associated, about twenty-five instrument men are employed, a shift system is run and

a member of the instrument repair staff is always present when a large unit is being brought on stream. In practice, with an experienced man, this strengthens the operating staff just at the time when it has to be strengthened, and it is a service greatly appreciated by the plant operators themselves.

The total instrument staff required in a refinery will depend to some extent on the part of the world in which it is situated, because in highly industrialized countries, particularly the U.S.A., instrument manufacturers can be depended upon to carry out a good deal of the major repair work that becomes necessary from time to time.

SOME APPLICATIONS OF METERING IN OILFIELD OPERATIONS.*

By Captain D. Comins, M.C., R.E. (retired),
M.Am.Inst.M.E. (Member).

Synopsis.

Owing to the trend towards primary processing of crude production on site, oilfields with their topping plants, stabilization plants or gasoline-recovery plants are tending to resemble refineries. Examples are quoted. Thus, routine applications of metering in oilfields—briefly outlined—are mostly the same as discussed in Mr. Adey's paper, and in all these, routine technique is similar except in detail, the only variables being in density and viscosity of fluid metered; in flowing pressure and temperature and in steadiness of flow.

A special technique is, however, necessary in measurement—in the broader sense of metering—of "live" crude production; *i.e.* of crude containing dissolved gas under pressure, with or without the free gas associated with it at the pressure of measurement. There are two salient operations in which this is required: in measuring the production rate or gas: oil ratio of a well which cannot conveniently be tested to an individual separator or tank; and in routine operation of multistage gas separation as a means of gasoline recovery, or, rather, of gasoline retention.

Comparatively little having been published on these specialized applications of metering, the body of the paper is a description of these as practised on the Iranian fields.

Points of emphasis are a detailed statement of apparatus and technique of the "Portable Tank and Gas Bags" method of estimating production and an outline of principles and operation of Multistage Gas Separation and of the rôle of metering in assessing the results achieved.

This description of special applications of metering is prefaced by a tentative discussion of the comparative accuracy of routine orifice metering and of tank dipping—a subject on which data from members' personal experience in different countries would be welcomed.

As suggested by its title, it is only proposed in this paper to discuss certain specialized applications of metering in oilfields, which may be of some interest in that comparatively little has so far been published regarding these. No attempt is made to discuss the many other routine applications of metering in oilfields or the details of operating and instrumental technique incidental to accuracy in such work, the latter being left to specialists on the operating and manufacturing sides.

As regards the former, owing to the modern trend towards primary processing of crude production on site, oilfields, with their topping plants and their stabilization plants or gasoline recovery plants, are tending more and more to resemble refineries. Examples which may be quoted are the Masjid-i-Sulaiman field in Iran, where, in the interests of flexibility in meeting market requirements with minimum pipe-line throughput, crude is processed as and when and how required and surplus products returned to the reservoir; and the Kirkuk field in Iraq, where, in order

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to retain the maximum amount of desirable light fractions and the minimum amount of undesirable light fractions in the crude for delivery to the long pipe-line to the Mediterranean, crude and dissolved gas production is stabilized under pressure [1]—an operation until recently confined to refineries. Similar plants are also in operation on the Basile field, Louisiana,[2] and in the Tepetate field, Louisiana.[3]

Thus the routine applications of metering in oilfields are mostly the same nowadays as those discussed in Mr. Adey's paper. As in the refineries, a number of different liquids and gases require to be metered—water for domestic purposes, boilers, or cooling towers; crude to process plants, or pipe-line; circulating oil in gasoline absorption plants; products and gasoline ex process plants; surplus products re-injected to reservoirs; steam to engines or turbines; lean gas ex crude separators; lean gas ex gasoline recovery plants; lean gas to boilers, engines or turbines; lean gas to repressuring of reservoirs; lean gas to domestic fuel; rich gas ex separators; rich gas ex crude process plants; rich gas to gasoline recovery plants; rich gas to regassing and rejuvenation of surplus products re-injected to reservoirs.

In all these jobs (the above catalogue of which does not claim to be comprehensive), the routine technique of metering is more or less identical, except in detail; the only variables to be taken care of being in the density and viscosity of the fluid to be metered; the temperature and pressure at which it is flowing; and the steadiness of flow. It is probably a safe generalization to say that the only oilfield operations in which a different technique is necessary from that in refineries, is in the metering of "live" crude production and in the measurement of mud fluid losses whilst drilling into a potential oil- or gas-bearing formation. By "live" crude is meant crude ex wells containing dissolved gas under pressure—such crude being either with or without the free gas associated with it at the particular pressure of metering.

The question of mud fluid losses may be dismissed very briefly. Its importance lies in the fact that appreciable losses indicate that favourable reservoir conditions have been encountered, the mud fluid running away into fractured or very porous formation. It also indicates that the pressure of mud fluid in the well exceeds the reservoir pressure and should be reduced in order to minimize the risk of sealing-off the formation. Conversely, of course, an increase in the rate of mud fluid return to surface indicates that a show of gas, oil or water, under higher reservoir pressure than that of the uncontaminated mud fluid, has been struck and is beginning to enter the bottom of the well. The method of measuring the mud fluid gains or losses is merely by dipping the level of mud fluid in the mud storage tank from which the mud is drawn and to which it returns after circulation.

Comparative Accuracy of Metering and Tank Dips.

Before going on to discuss measurement of "live" crude production—which is the main objective of this paper—this may be a suitable moment to raise a point of very considerable interest in the oil industry and, of course, to meter manufacturers, in the hope of provoking profitable dis-

cussion on the subject. I refer to the relative accuracy of orifice metering as compared with tank dipping.

It is probably common ground that metering has been adopted by most oil companies for their internal operations on producing fields, pipelines and refineries, as being far cheaper and more convenient than tank dipping and as being sufficiently accurate for all practical purposes and for internal balance sheets of crude, gas and products. It may indeed be claimed that the accuracy obtainable by good metering—all technical precautions being taken—is of the same order as that obtained in tank dipping, where the latter is not scientifically controlled.

Although on the face of it tank dipping would appear to be one of the simplest of oilfield operations, there are various factors which make for inaccuracy unless very precise quantitative corrections for these are made. This is a subject in itself; but amongst these factors may be mentioned the variation in cross-section of the tank itself, the measurement of the average temperature of the tank at the time of measurement, the sampling of the crude for determination of the average specific gravity in the tank, and the correction of the volume of the oil from that at the temperature of measurement to that at a standard temperature such as 60° F. Of these, the last is the most difficult correction, particularly with waxy oils, with which it is understood that standard routine correction for temperature may be very inaccurate and special precautions are necessary.

There is, however, no question that tank dipping, when such factors are properly taken care of on a scientific basis and all technical precautions observed, is definitely more accurate than metering over any comparatively short period of test.

One is on more debatable ground in attempting to put these statements on a quantitative basis. As a starting-point for discussion, $\pm$ 1 per cent. for metering with all technical precautions taken, a similar or perhaps slightly better figure for ordinary tank dipping, and $\pm \frac{1}{2}$ per cent., or even, possibly, $\pm \frac{1}{4}$ per cent., for tank dipping under precise scientific control, are suggested—all these figures being applicable to comparative short-period tests. (The $\pm$ 1 per cent. figure for metering given above refers, of course, to liquids, the comparison being with tank dips. For gases the accuracy of metering under best conditions is generally accepted to be about $\pm$ 2 per cent.)

Where tonnage in tanks is directly calculated from readings of a mercury column connected to the bottom of the tank through a seal, the comparative accuracy of tank figures is still greater; as, in this method, the conversion of volume into weight, which is one of the major sources of inaccuracy in the calculation of tonnage figures from actual tank dips, is automatically avoided.

As tonnage rather than volumetric figures are the rule for fiscal and sales purposes, it is likely that this method of tank measurement will be increasingly adopted. In fact, the author is informed by the Iraq Petroleum Company that, in agreement with the Iraq Government, they have recently installed this method for fiscal purposes.

Over long periods the difference between the relative accuracy of metering and of tank dipping should be even less than between the figures quoted above, provided that " systematic " errors are reduced to a minimum

in both methods. "Systematic" errors are referred to in the sense used by Mr. E. S. L. Beale—who has made a deep study of the physical and mathematical technique of both metering [4] and tank dipping [5]—as being errors which will not tend to cancel themselves out over a long period or a large number of observations, as will errors of visual observation or approximation. Such "systematic" errors may be due either to approximate methods of calculation and to approximations in the mathematical constants employed—both of which sources of error are clearly avoidable; or to error in initial calibration—*e.g.* in tank dipping—of the tank itself; or, in orifice metering, of the orifice itself, particularly when metering viscous liquids. In orifice metering further sources of "systematic" error are faulty instrumentation and corrosion of wear of the orifice.

In orifice metering the initial calibration of the orifice is, of course, the most important factor, and a far greater degree of accuracy can be obtained where one definite product (or crude) is metered by a given instrument and the orifice is calibrated on site for this product against scientifically controlled tank dips.

Supporting the generalizations made earlier regarding the attitude of oil companies to metering, and the relative accuracy of metering as compared with tank dips, the following evidence may be quoted :—

(*a*) In a recent description [6] of the development work of the Mexican Eagle Company on the Poza Rica field, Messrs. Clark and Flinn, the Company's Chief Exploitation and Mechanical Engineers respectively, state :—

> "The system of gauging by flow meter has proved entirely successful in Poza Rica, the average difference between the total volume or production as obtained by metering and by gauging in main storage tanks being in the neighbourhood of one quarter of one per cent. over the past year. It is in fact generally considered that any error more probably lies in the tank gauging. When it is considered that for these wells 5000-barrel tanks would normally be necessary for each well if measurement by gauge tanks were resorted to, and that equal accuracy in measurement by metering has been obtained at a cost of about $500 per well, some idea of the saving in equipment and operating cost may be realized. It is hoped, with the master meter and meters on the main pipe-lines leading out of the district, that tank gauging may eventually be entirely eliminated."

(*b*) In a recent communication to the author, Messrs. George Kent state that they have carried out several lengthy tests in both Mexico and Roumania, following which the method of measurement by meter instead of by tank has been accepted in certain instances. The same firm have submitted data of further tests carried out on crude oil measurement. In these, on individual short tests, the divergence between meter and tank-dip results was usually of the order of $\pm$ 1·0 per cent., but in three tests which were repeated over a period of several days the mean divergence was well below this figure.

(*c*) In Iran the Anglo-Iranian Oil Company rely on metering throughout their internal operations. Tank dips are used for

measurement of crude and products sold or exported. (The figures obtained for the latter by tank dips normally tie in within ± 1·0 per cent. to 1·5 per cent. with those determined by meter. In cases where the meter has been previously calibrated on site against scientifically controlled tank dips, the difference is, however, negligible.)

(*d*) The American Gas Association, as a result of exhaustive investigations, have reported [7] the tolerance of discharge coefficients for orifice plates, when carefully designed and accurately made, to be ± 0·5 per cent. for liquids, and that "for commercial work the tolerances must include some allowance for the pressure and temperature measuring devices as well as that for the orifice plate, and so the commercial accuracy will be somewhat less."

Similar data from other countries and oil companies would be welcomed in the discussion.

Metering "Live" Crude.

Reverting now to the subject of metering "live" crude, there are two salient operations in which this is essential; in estimating the production rate or the production rate and producing gas–oil ratio of a well which for some reason cannot be satisfactorily or conveniently tested to an individual separator and/or tank; and in the routine operation of multi-stage gas separation as a means of gasoline recovery, or, rather, of gasoline retention. Each of these cases will be discussed in turn.

The necessity or desirability of the first may arise when a well is first brought in and an estimate of crude and gas production capacity at varying flowing pressures is desired before deciding on the capacity of separators or tanks to be installed, or on whether further deepening or possibly acid treatment is indicated. It may also arise when a similar survey of a completed well is desired, but the production lay-out is such that isolation of the production is impracticable. Repeat surveys of this nature are desirable at intervals dependent on the rate at which reservoir pressure and reservoir saturation pressure are dropping in the particular field concerned.

In the Iranian fields the earliest attempt to solve this problem was by the method which, as a matter of mainly historical interest, is illustrated on page 145.

A station is selected on the production line where the flowing pressure is as low as possible and yet steady and the line is tapped for a static pressure gauge and a Pitot tube 10 in. down-stream, which is arranged to work through a gland. The Pitot tube is first connected to the vertical cylinder shown and a rough approximation to the gas–oil ratio (at actual line pressure) obtained by flowing to the cylinder until a pressure just below static line pressure is built up in it. The H.P. manometer shown is then connected to the Pitot tube and the static pressure gauge connection and the differential pressure measured. Knowing the approximate gas–oil ratio at the pressure in the line, the head of fluid represented by the differential pressure may be calculated and thus the total flow of fluid, by ordinary Pitot tube formula. This total flow is then allocated between oil and gas in the proportions of the gas–oil ratio observed. The

APPARATUS FOR PRODUCTION TEST
[METHOD OF MAKING ROUGH ESTIMATE OF RATE OF FLOW OF LIVE CRUDE (WITH FREE GAS) THROUGH A PIPE LINE.]
MANOMETER
PITOT TUBE
THERMOMETER
(i) MANOMETER CONNECTIONS
PROPORTIOMETER
THERMOMETER
(ii) PROPORTIOMETER CONNECTIONS.

FIG. 1.

operation is repeated for varying depths of insertion of the Pitot tube into the line and the results averaged.

Estimation of production by this method is usually accurate within ± 10 per cent. on wells flowing steadily, where the line is reasonably small for the production and therefore full of a comparatively homogeneous mixture of oil and gas. In surging wells or in lines where layering of the oil and gas is excessive, very large errors are possible—± 25 per

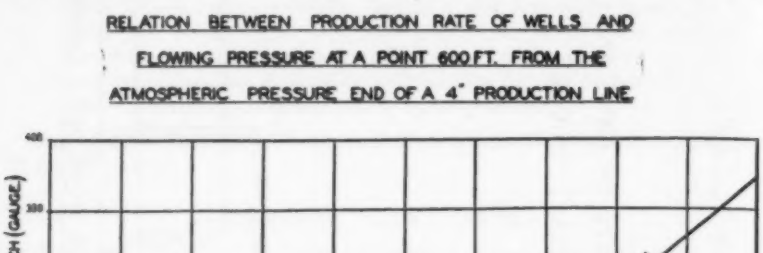

RELATION BETWEEN PRODUCTION RATE OF WELLS AND
FLOWING PRESSURE AT A POINT 600 FT. FROM THE
ATMOSPHERIC PRESSURE END OF A 4" PRODUCTION LINE
FLOWING PRESSURE 600' FROM OPEN END LBS./SQ. INCH (GAUGE)
PRODUCTION RATE (SINGLE FLASH) IN MILLIONS OF GALLONS/DAY
IN FIELD WHERE AVERAGE PRODUCING GAS-OIL RATIO (SINGLE FLASH) IS APPROX. 90:1
DITTO WHERE AVERAGE G.O.R. IS APPROX. 40:1

FIG. 2.

cent. and more. For these reasons and because the procedure of measuring the gas–oil ratio is not scientifically correct (though it yields reasonably good results as a first approximation), the method has been suspended, but, being very simple both in construction and operation, may prove useful for rough preliminary estimates in cases where other facilities are not for the moment available.

A very simple method of estimating well productions (but not gas–oil ratios), which has been developed in Iran and is still in routine use, is based on line pressure drop, under conditions where no gas is separated above atmospheric pressure. It is only applicable in areas where the

producing gas–oil ratios of all wells are known to be approximately the same and do not change appreciably over a reasonable period of time. This is the case on the Iranian fields, where the saturation pressure of the reservoir crude is known in the different areas and only drops very slowly with time. The method is purely empirical, working graphs, of which examples are shown in the next figure, being constructed from observed pressure and production data of a number of wells. As a routine, the flowing pressure is observed at a point 600 ft. from the atmospheric pressure end of a 4-in. production line.

On fields where reservoir saturation pressures fall fairly rapidly with production, similar graphs would require to be revised from time to time. The accuracy is, of course, dependent on the constancy of gas–oil ratio, but is quite good enough for the purpose of preliminary estimates, an error of more than $\pm$ 10 per cent. being unlikely if the flowing pressure is reasonably steady.

Portable Tank and Gas Bags Method.

For accurate measurement of well productions and producing gas–oil ratios at varying rates of flow, when production to individual separators and/or flow-tanks is impracticable or undesirable, a method has been developed and used for some years on the Masjid-i-Sulaiman field, Iran, in which the total oil and gas production of the well is by-passed for a very short time to a portable tank fitted with gas bags. Results obtained have been proved to be accurate within about $\pm$ 1·0 per cent. by check measurements of oil and gas productions when flowing at the same rate to full capacity tanks. This method has already been briefly described [8] by Mr. L. A. Pym, but it is thought that a more detailed description may be useful to any operators who may contemplate using similar apparatus.

The lay-out is self-explanatory from the semi-perspective sketch shown in Fig. 3, which, by the way, is roughly to scale.

Working across the sketch from the well on the right, the main points regarding equipment to which attention may be drawn before describing operating procedure are :—

1. The Halliburton outfit mounted on a light truck, which is there for the purpose of lowering a bottom-hole pressure indicator into the well to a point opposite the main oil show in order that the bottom-hole static pressure with the well shut in may be observed, and also the bottom-hole flowing pressure at the different rates of flow to be tested.

2. The removable portion of the normal production line consists of one joint which is left flanged for insertion of the special section shown in the sketch. This section, which may be inserted any time before the actual tests, includes orifice connections to the meter shown, and a Y piece with instantaneous operating valves and setting valves for diverting flow from the production line to the tank without changing the rate of flow.

3. The orifice meter is for differential pressure readings only, in order to ensure that flow when diverted to the tank is at the same rate as when flowing in the line. If it is not, the setting valve to the tank is adjusted accordingly. The orifice plate is chosen so that at the full rate of flow there is a high reading of the meter in order that the orifice need not be changed for lower rates of flow.

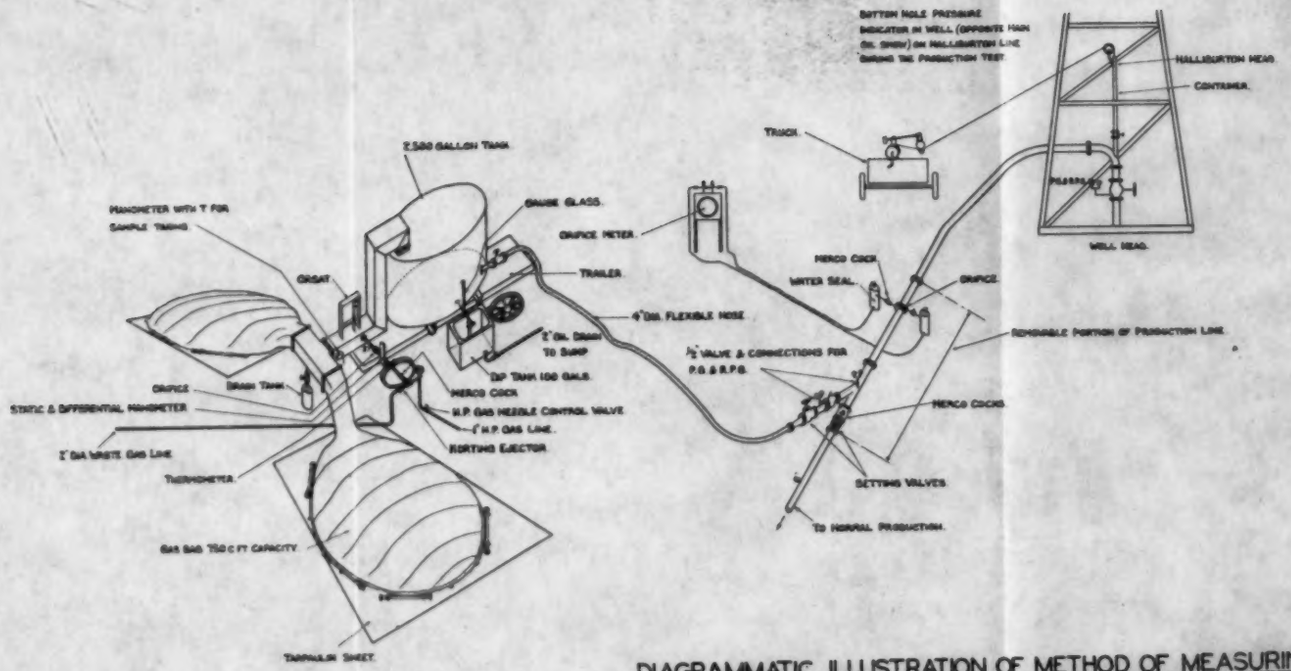
Whilst on this point, it may be mentioned that interchangeable orifice fittings are now in very general use in orifice metering in circumstances where it is desirable to be able to change an orifice plate without interrupting flow. (In the Kent fitting the plate carrier can be withdrawn into an upper chamber, which is then isolated from the pipe by a cock, following which the upper carrier can be removed and the plate changed. This fitting avoids the necessity of using by-pass valves, thus saving money and space.)

4. The tank, which is permanently mounted on a trailer, complete with rectangular tank duct (24 in. × 15 in.), is about 2500 gallons capacity and about 5 ft. in height. (When not in use all tank connections, *i.e.* inlet, drain, and gas ducts, should be blanked off to prevent inlet of air.) The tank, and especially the 100-gallon dip tank for draining off and measuring the amount of crude delivered to the tank, should be carefully levelled before the test. A gauge glass is provided with a mark by which the initial level of the oil may be set to the same level (in the nipple above the drain valve of the main tank) before each run. If the tank were completely emptied, gas would escape with the last oil being drained for measurement. The amount of oil going into the tank at Masjid-i-Sulaiman gas–oil ratios is about 200 gallons, this supplying sufficient gas to fill the bags.

5. The gas bags, which are of about 750 cub. ft. capacity each when inflated a reasonable amount, *i.e.* about 2 ft. to 2 ft. 6 in., in the middle, are made of flax canvas, 21 oz. to the square yard, double compromium proofed, wax finish. When new, each bag is treated with about 20 gallons of No. 340 lubricating oil and the upper face of each bag is treated with about 7 gallons (1 drum) after each job, the faces being reversed each time. When soaked, the bags weigh about half a ton each and roll up for transport into bundles about 5 ft. long by 3 ft. diameter. They are protected from being holed by lying on tarpaulin sheets about 30 ft. × 30 ft., the ground beneath the sheets being carefully cleared of stones. The workmen are only allowed to walk on the bags in bare feet. Loops are provided on the bags for weighting them down with pipe on the windward side.

6. The throats of the gas bags are supported by a wire frame to keep them open and the necks at the end of the throats are of quadruple material with eyelet holes punched every 3 in. The connection to the gas duct is made by means of a flange through which the throat of the gas bag is threaded, turned up, and clamped between this flange and the end flange of the tank by bolts through the eyelet holes.

7. The high-pressure gas line shown is for the purposes of operating the Korting ejector, which deflates the gas bags at a steady rate through the 2-in. evacuation line on the horizontal gas duct. During preliminary runs the H.P. gas pressure on the Korting ejector is adjusted to give the maximum rate of evacuation of the bags as indicated by the differential pressure across the orifice in the 2-in. line, which is recorded by the water manometer shown. The H.P. gas pressure required is usually of the order of 100# to 150#, but varies according to the length and arrangement of the waste gas line. At the optimum pressure the fluctuations in the differential pressure are negligible. The exhaust line should be as straight and short as possible.



DIAGRAMMATIC ILLUSTRATION OF METHOD OF MEASURING PRODUCTION & GAS: OIL RATIO OF WELLS BY PORTABLE TANK & GAS BAGS.

SCALE.

FIG. 3.

[To face p. 148.

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8. The manometer on the gas duct itself is to show when evacuation of the bags is complete, a partial vacuum being indicated. The T off this for sampling is in order that the specific gravity of the gas may be determined (by weighing of flash samples) and the H_2S content (or rather the acid gas content) measured in the Orsat apparatus shown on the horizontal duct.

Before describing the procedure of the test, attention is drawn to the photographs of the equipment shown in Figs. 4–8.

The procedure in any given test, after completing the hook-up and preliminary preparations as mentioned above, is :—

1. With the valves on the Y to portable tank closed and well flowing at maximum rate, note the following :

(*a*) Well-head flowing pressure on both the pressure gauge and recording pressure gauge at the well.

(*b*) Line flowing pressure on both the pressure gauge and recording pressure gauge on the junction of the Y piece.

(*c*) Differential pressure on the recording orifice meter.

Wait till these are steady.

2. Close ½-in. blow-off cock between the main Merco cock to tank and the tank setting valve.

3. Set tank setting valve at probable number of turns open for production rate to be tested—a matter of experience.

4. Close meter valves. Unroll gas bags.

5. Simultaneously open Merco cock to tank and close Merco cock to normal production for a few seconds and note flowing pressures on the Y-piece junction and the differential pressure at the orifice meter (opening meter valves for purpose—if they are open during actual switch there will be a kick).

6. If the flowing pressure and differential pressure have changed, adjust tank setting valve accordingly and repeat process until they are approximately the same when flowing to tank as when flowing to normal production line.

7. Run in bottom-hole pressure indicator to main oil show and obtain readings of the bottom-hole flowing pressure and temperature at this rate of flow.

Note.—The bottom-hole pressure indicator should never be in situ in well during switches over from production line to tank, as the kick may affect it unless it is at least 500 feet off bottom. It is possible to run it in whilst well is flowing, except in big producers in small casing, in which case it must be *started* in with well shut in.

8. Whilst this is going on, the tank is emptied by draining to dip tank down to the mark on the gauge glass; the dip tank is emptied to within ½ in. of bottom and the gas bags are evacuated by turning on the H.P. gas to the Korting ejector, the bags being rolled up as they deflate. During this the Merco cock to the tank is, of course, closed. The tank setting valve is left open.

9. The first test run to the tank may then be made, the time of switching over the Merco cocks being noted by stop-watch. Flow to the tank

is continued until the gas bags are reasonably inflated (they have been unrolled again before starting the test), that is until they are about 2 ft. to 2 ft. 6 in. from ground in the middle. This takes anything from, say, 30 seconds to 5 minutes, depending on the size of the well. During this time the flowing pressures and differential pressure are again noted.

10. Switch production back to line—noting time with stop-watch. Close tank setting valve and open the ½-in. blow-off valve between the Merco tank cock and the tank setting valve (to prevent any gas leak from line to tank whilst gas bags are being deflated).

11. Open 1-in. H.P. gas valve, ½-in. Korting ejector valve, and 2-in. cock on the gas evacuation line from the gas duct and deflate bags. Note time of beginning and end of deflation (as this is required for making bag leakage allowance later). During deflation the following observations to be made :—

(*a*) On the manometer on the 2-in. gas evacuation line—periodically—the static pressure and the differential pressure across the orifice (1½-in. orifice usually suitable), also the temperature in the line.

(*b*) Samples of gas are collected from the connection in the horizontal duct and specific gravity and H_2S content determined.

(*c*) The oil is run off and measured in the small tank (two or three fillings being usually necessary), and its specific gravity and temperature measured.

Deflation may take on the average about three-quarters of an hour. During deflation the well is throttled-in in preparation for the next test at a lower rate of flow.

12. All tests are repeated at approximately two-thirds full flow (as determined by the differential pressure on the recording orifice meter) and at a lower rate of flow in order to give a point near the top of the steep portion of the flowhead-pressure production curve. (They are done in this order because the bottom-hole pressure indicator is a maximum reading instrument.)

13. After making the last test, it is repeated, but the gas bags are not deflated until next day. The gas–oil ratio determined next day is less, on account of bag leakage, and, the exact period of standing being known, this difference is applied on a proportionate basis to correct the actual gas–oil ratios determined for the slight leakage during deflation in the actual tests.

14. The well is closed in and the static bottom-hole pressure and temperature are measured with the bottom-hole pressure indicator. A bottom-hole sample taker is then run in and two bottom-hole pressure samples collected for determination of the saturation pressure and dissolved gas content of the reservoir crude, the latter being compared with the producing gas–oil ratios measured.

15. All pressure gauges and recording pressure gauges are calibrated against a dead weight tester over the range of observations made. Barometric pressure on each day is observed and the ground elevation of the well noted for use in calculations converting gas volumes to S.T.P.

From the data described above, all the information required

from the well can be calculated. Taking the minimum period of test as about 30 seconds (at least 1 minute is desirable to attain the accuracy mentioned of ± 1 per cent.) the tank and bags are capable of handling a gas production of about 4 m.c.ft./day, which, at Masjid-i-Sulaiman gas–oil ratios, represents about 600,000 gallons of crude a day, the crude-rate capacity varying, in different fields, of course, with the producing gas–oil ratio. Larger capacity apparatus could be made on the same principles, but that described is approaching the limits of convenience in handling and transport.

The type of data obtained is illustrated in the next two figures :—

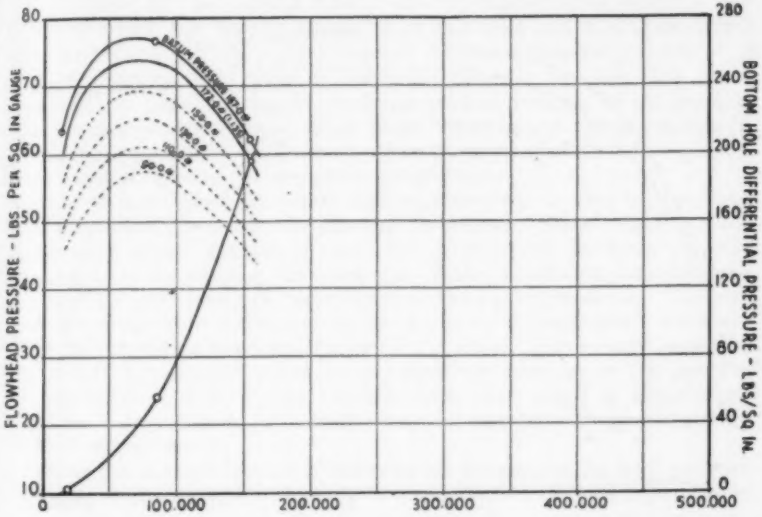

FIG. 9.

SURVEY DATA FROM A MODERATE WELL.

Production (gallons per day).	Flowhead Pressure (lb./sq. in. gauge).	B.H.D.P. (lb./sq. in.).	Bottom-Hole Temp. (° F.).	Gas-Oil Ratio (at a temp. of separation of 80° F.).	Percentage H_2S in Gas (at a temp. of separation of 80° F.).	Specific Gravity of Gas (at a temp. of separation of 80° F.).
155,000	62	197	96·2	42·2	11·4	—
84,500	77	54·5	96·2	42·6	—	—
15,400	63	1	96·0	43·5	—	—
0	—	0	96·1	—	—	—

Flowhead elevation	10,844
Elevation of main limestone	8,569
Position of shows	{8,558 {8,502
Casing diameter (in.)	6·776
Date of tests	28/4/34
Datum pressure at date (lb. per sq. in. absolute)	187
Saturation pressure (lb. per sq. in. absolute)	578
Elevation of bottom-hole measurements	8,497
Static bottom-hole pressure (lb. per sq. in. absolute)	687·5

This paper is hardly the right medium in which to discuss the significance of these data. Attention may, however, be drawn to one point, the steepness of the (lower) curve relating bottom-hole differential pressure (the difference between bottom-hole static pressure and bottom-hole flowing pressure) in the smaller well, as compared with its flatness in the larger well. This indicates that the comparatively small production capacity is due to poor reservoir connection and not to lack of available energy in the reservoir crude. In such circumstances acid treatment is indicated as desirable and has frequently been successful in converting a well of characteristics shown in Fig. 9 into one of characteristics shown in Fig. 10.

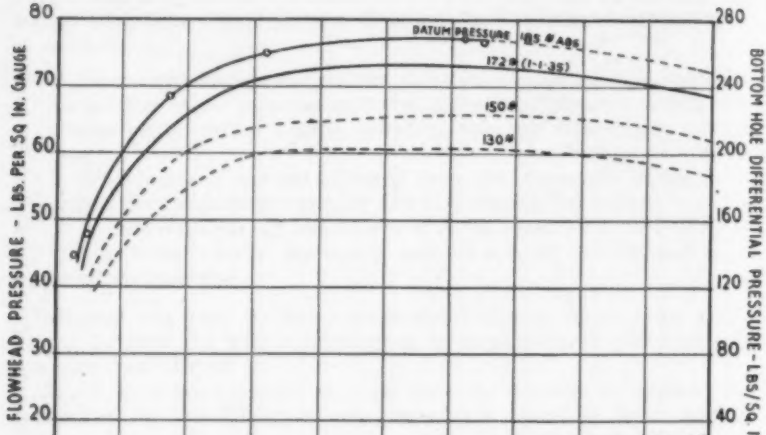

FIG. 10.

SURVEY DATA FROM A GOOD WELL.

Production (gallons per day).	Flowhead Pressure (lb./sq. in. gauge).	B.H.D.P. (lb./sq. in.).	Bottom-Hole Temp. (° F.).	Gas-Oil Ratio (at a temp. of separation of 80° F.).	Percentage H_2S in Gas (at a temp. of separation of 80° F.).	Specific Gravity of Gas (at a temp. of separation of 80° F.).
318,000	76·5	—	—	39·2	—	1·149
306,000	77	12·5	—	40·8	—	—
182,000	75	3·5	—	40·4	10·6	—
92,500	69	—	—	42·3	—	1·153
21,500	47	1	90·2	42·7	—	—
13,000	44	—	—	43·8	—	1·143
0	—	0	90·2	—	—	—

Flowhead elevation	10,978
Elevation of main limestone	9,119
Position of shows	9,078, 9,045, 9,001
Casing diameter (in.)	8·291
Date of tests	8/5/34
Datum pressure at date (lb. per sq. in. absolute)	185
Saturation pressure (lb. per sq. in. absolute)	489
Elevation of bottom-hole measurements	9,039
Static bottom-hole pressure (lb. per sq. in. absolute)	525

METERING IN MULTISTAGE GAS SEPARATION PROCESS OF GASOLINE RECOVERY.

Coming now to the metering of "live" crude in multistage gas separation: before discussing detail it may be advisable to describe in general terms this rather novel system of gasoline recovery, or, rather, retention. The physics and mathematics of the process have been dealt with by Dr. C. J. May in a paper [9] before the World Petroleum Congress in Paris last summer, but so far only the synopsis would appear to have been printed. (Dr. May with Mr. H. S. Gibson, Assistant Fields Manager (Production) in the Iranian fields, was responsible for developing this process, which has been in operation on the Haft Kel field since 1930.) The underlying principles may, however, be stated reasonably briefly.

The objective is to retain in the liquid phase in the flow tank crude delivered to pipe-line the maximum proportion possible of the gasoline components of the reservoir crude, these remaining, of course, entirely in the liquid phase until the pressure of the reservoir crude is reduced below its saturation pressure at any given temperature.

It is an established fact—and there is, therefore, no need to enter into the theoretical reasons for it—that as the pressure of the reservoir crude is lowered below its reservoir saturation pressure, *e.g.* by flow in a well, the lighter hydrocarbons, methane and ethane, invariably constitute the bulk of the gas coming out of solution at the higher pressures. The proportion of lighter hydrocarbons in the gas evolved progressively decreases and the proportion of potentially useful "gasoline" components, propanes (? useful), butanes and pentanes, progressively increases as the pressure of the crude is reduced, the increase being very rapid as atmospheric pressure is approached. ("Gasoline" is used in a general sense. Actually it is an elastic term.)

Now, for a condition of equilibrium to be reached at any pressure between crude and gas with which it is in contact, *e.g.* in a separator or in a tank, the partial pressure of each individual component—let us in future consider, say, butane only—in the liquid phase, must equal the partial pressure of that component in the gaseous phase, and, until such equilibrium has been reached, the butane will continue to come out of solution from the crude, thereby robbing the crude of some of its potential gasoline content. Once equilibrium has been reached, the crude is stable for those particular conditions of pressure and temperature as long as it is in contact with the same gas.

The actual amount of butane which is required to be evolved from the crude to build up the butane partial pressure in the gas space is, however, greatly reduced if the *proportion* of butane in the total gas already in contact with the crude has been increased by previous removal of lighter hydrocarbons at a higher pressure stage of separation.

The reason for this is that the partial pressure of the butane in the gaseous phase, being the actual pressure of separation × the percentage by volume of butane in the total gas (making the necessary allowances for deviations from Boyle's Law), is very considerably affected by removal of other constituents of the gas in earlier stages of separation; whereas the

partial pressure of the butane in the liquid phase, being the vapour pressure of butane at the temperature of separation × the mol fraction of the butane in the crude, would be constant for any given pressure and temperature of separation, were it not for the extra retention of butane in the crude, resulting from the process.

The same process is repeated at each successive pressure stage of separation until atmospheric pressure is reached, the net effect being a stabilized crude (providing, of course, it is in contact with its own flow tank gas), which is of lighter gravity and contains more gasoline than single flash crude.

The process may, of course, be completed at a higher pressure than atmospheric pressure—say 10# gauge—in which case gasoline retention is greater, but the crude must be retained at that pressure through the pipe-line and until actually handled in the refinery.

A simple non-technical way of explaining the process is to visualize a well as producing neat gasoline only with a large quantity of air. It is easy to see that if one were to separate off the bulk of the air at high pressure much less gasoline would evaporate than if the air were delivered to the tanks.

The diagram (Fig. 11) illustrates the process and results obtained.

It will be noted that the bulk of the methanes and ethanes are removed in the first two stages of separation. A point to which attention should be directed is the decrease in liquid volume of the crude at each separation stage, as this has to be taken into consideration in the metering. This point will be returned to later.

The diagram (Fig. 12) illustrates the increased recovery of gasoline constituents by multistage separation as compared with single flash production to tank at atmospheric pressure. Gasoline, being an elastic term, is not specifically referred to as such, Fig. 12 showing the retention of grouped constituents.

The increased volumetric production of crude in the case of multiseparation will be noted, the increase being mainly represented by pentanes, butanes and propane. The large reduction in producing gas–oil ratio will also be noted. A point that should be appreciated is that, although in Fig. 12 the comparison is made at atmospheric pressure, the multistaged crude can be delivered direct to pipe-line from the 10#, or even the 20#, separators, thus delivering an even greater proportion of pentanes, etc., to the refinery. By multistaging to 10# the extra retention of gasoline components is of the same order as the recovery obtained by processing the whole of the single flash gas production in 35# absorption plants.

Fig. 13 shows the general lay-out of a multiseparation scheme and illustrates the use of meters and automatic control equipment. The sketch is self-explanatory, but certain points having a bearing on metering may be brought out :—

1. Crude production from the individual wells can only be metered at the well-head separators (at the outlet of course) as it passes thence to the central battery. At the well-head separators, as will have been noted from Fig. 11, the actual liquid volume is substantially greater than it is by the time it reaches the communal metering point on the pipe-line after

DIAGRAMMATIC ILLUSTRATION OF MULTISEPARATION PROCESS OF GASOLINE RECOVERY

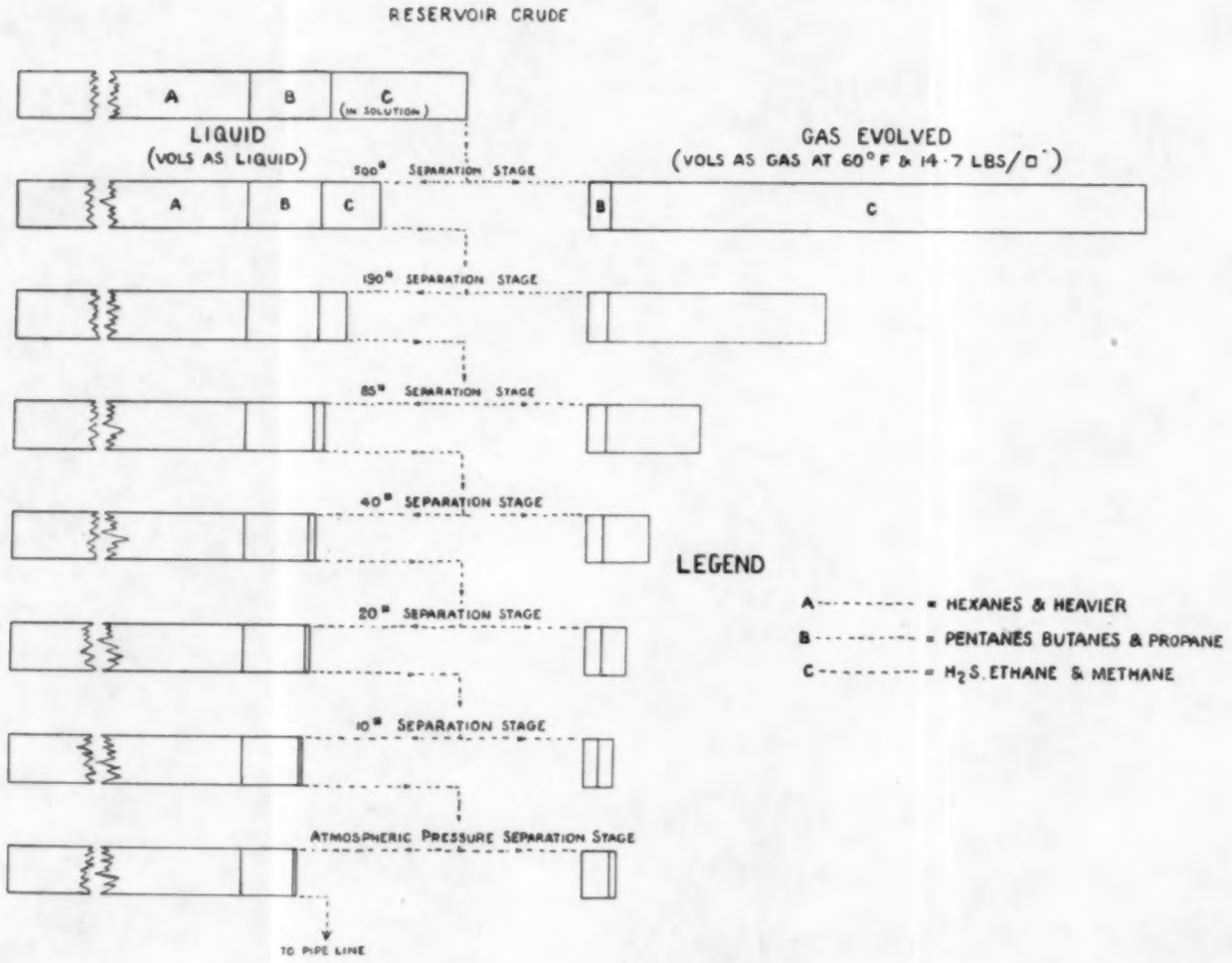

FIG. 11.

[To face p. 185.

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DIAGRAMMATIC ILLUSTRATION OF EXTRA GASOLINE RECOVERY BY MULTISEPARATION AS COMPARED WITH SINGLE FLASH SEPARATION.

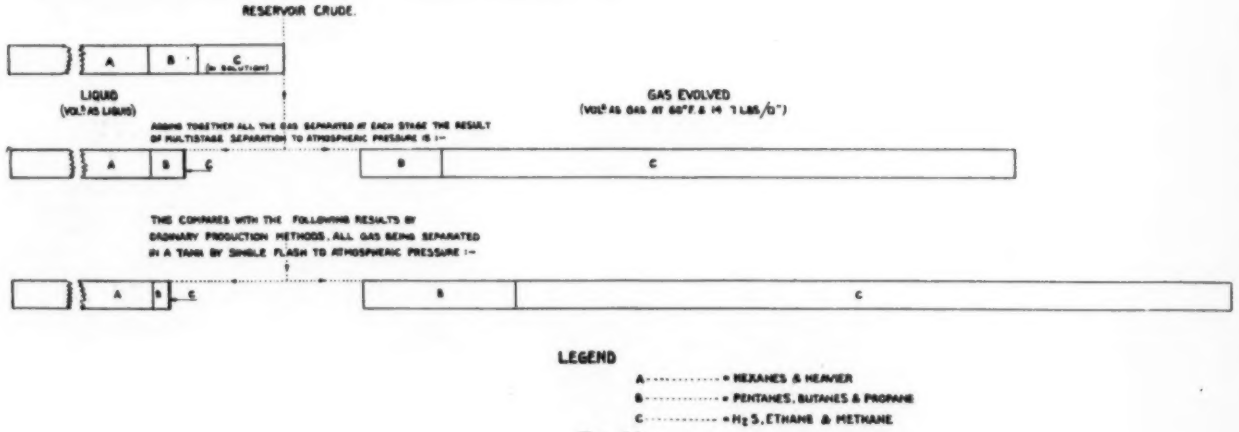
RESERVOIR CRUDE.
A
B
C
(in Solution)
LIQUID
(VOL.S AS LIQUID)
GAS EVOLVED
(VOLS AS GAS AT 60°F. & 14·7 LBS./□")
ADDING TOGETHER ALL THE GAS SEPARATED AT EACH STAGE THE RESULT OF MULTISTAGE SEPARATION TO ATMOSPHERIC PRESSURE IS :-
THIS COMPARES WITH THE FOLLOWING RESULTS BY ORDINARY PRODUCTION METHODS, ALL GAS BEING SEPARATED IN A TANK BY SINGLE FLASH TO ATMOSPHERIC PRESSURE :-
LEGEND
A ..... = HEXANES & HEAVIER
B ..... = PENTANES, BUTANES & PROPANE
C ..... = H_2S, ETHANE & METHANE

FIG. 12.

reduction to atmospheric pressure. The communal total and the sum of the individual totals, therefore, require to be reconciled.

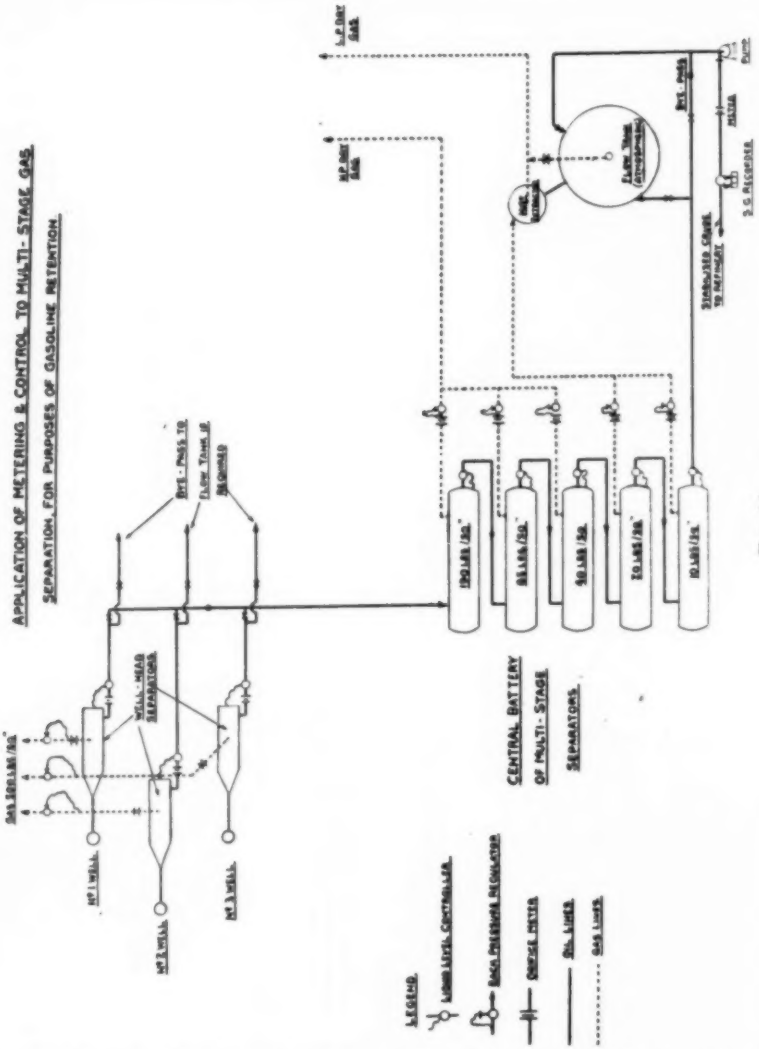

FIG. 13.

2. The gas off the separators is metered at the pressure of the separators for greater accuracy. Allowance must, therefore, be made for deviation from Boyle's Law, which is considerable.

3. The object of the various metering operations is, in combination

FIG. 4.

PHOTOGRAPH OF Y PIECE, VALVES AND ORIFICE FITTINGS.

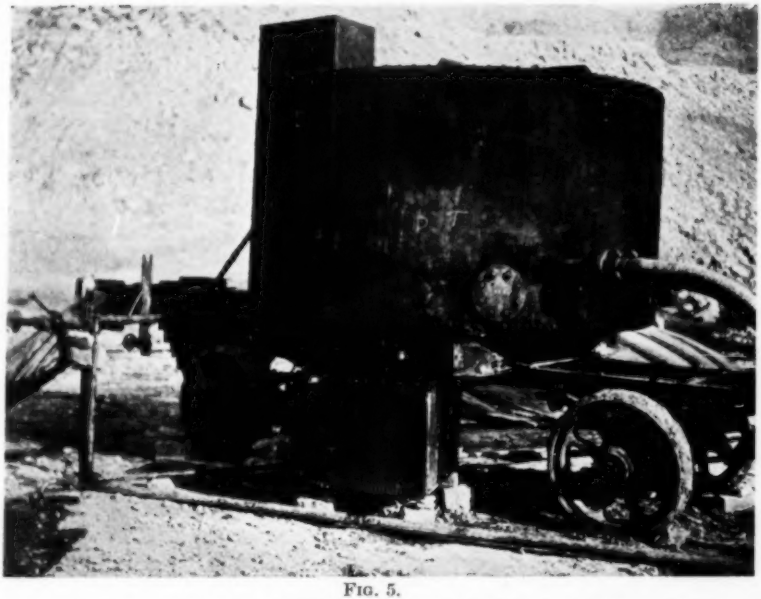

FIG. 5.

PHOTOGRAPH OF THE MAIN TANK SHOWING DIP TANK, GAUGE GLASS AND TANGENTIAL INLET.

[*To face p.* 156.

FIG. 6.

PHOTOGRAPH SHOWING GAS BAGS INFLATED AND GENERAL LAY-OUT.

FIG. 7.

PHOTOGRAPH SHOWING THROAT OF GAS BAGS' CONNECTION TO GAS DUCT, H.P. GAS LINE AND KORTING EJECTOR.

FIG. 8.

PHOTOGRAPH SHOWING ORIFICE, STATIC AND DIFFERENTIAL MANOMETER, THERMOMETER AND CONTROL COCK IN THE 2-IN. GAS EXHAUST LINE FROM GAS DUCT. (ALSO SHOWS FURTHER VIEW OF EJECTOR ARRANGEMENTS.)

FIG. 14.

PHOTOGRAPH OF H.P. WELL-HEAD SEPARATOR.

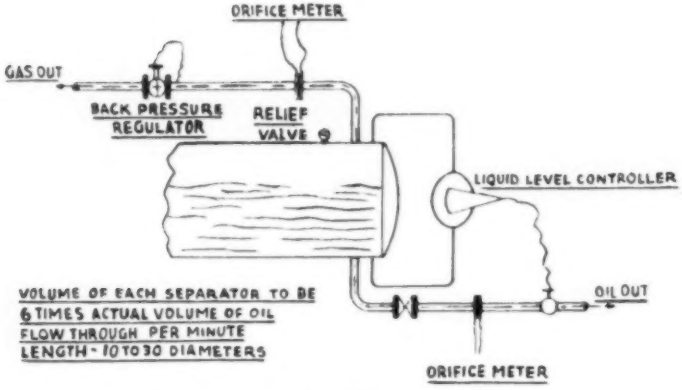
ORIFICE METER
GAS OUT
BACK PRESSURE REGULATOR
RELIEF VALVE
LIQUID LEVEL CONTROLLER
OIL OUT
VOLUME OF EACH SEPARATOR TO BE 6 TIMES ACTUAL VOLUME OF OIL FLOW THROUGH PER MINUTE
LENGTH - 10 TO 30 DIAMETERS
ORIFICE METER

FIG. 14A.

SKETCH ILLUSTRATING METERING AND CONTROL ON TYPICAL WELL-HEAD SEPARATOR.

Note.—Central battery separators are exactly similar in design, but of larger dimensions to suit throughput, and oil meter is omitted at the individual stages.

FIG. 15.

PHOTOGRAPH OF CENTRAL BATTERY OF SEPARATORS.

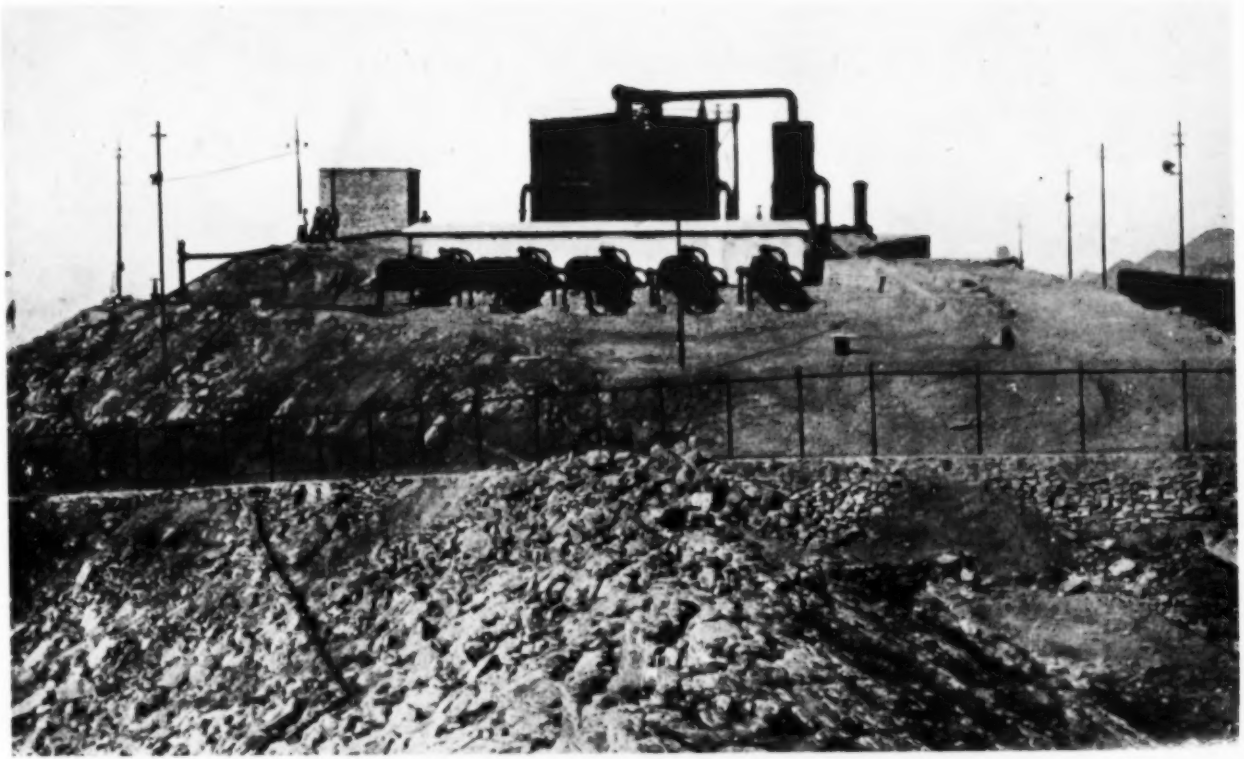

FIG. 16.

PHOTOGRAPH OF CENTRAL BATTERY AND FLOW-TANK UNIT.

FIG. 17.

PHOTOGRAPH OF SPECIFIC GRAVITY RECORDER.

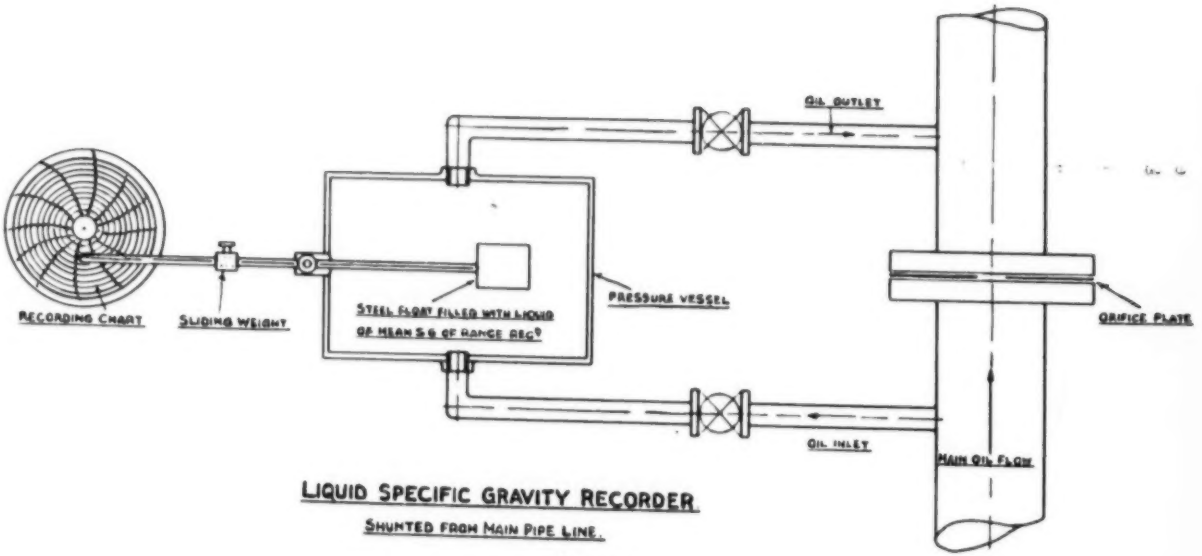

FIG. 17A.

SKETCH ILLUSTRATING WORKING PRINCIPLE OF CRUDE SPECIFIC GRAVITY RECORDER.

with analyses of the gases and crude at the different stages, to enable a balance sheet to be drawn up, on the lines of diagrams Nos. 11 and 12, thus ensuring maximum efficiency of operation.

4. The multistaged crude is not suitable for tank dipping except in pressure tanks, as a proportion of the extra gasoline constituents retained by the process would be lost by evaporation. It is, therefore, preferable to meter the multistaged crude. Consequently, to avoid pulsation and ensure accuracy in metering, centrifugal pumps should be used for delivery to refinery rather than reciprocating pumps.

5. A continuous record of the specific gravity of the crude piped to refinery is essential, as a reduction of over 1½ per cent. in specific gravity may be practicable by multistaging to 10# instead of single flashing to atmospheric pressure.

Figs. 14–17A are of interest in connection with the points generally discussed above.

A small proportion of the flow in the pipe-line is shunted through the pressure vessel of the recorder, inside which is a float filled with a liquid of the mean specific gravity of that to be recorded. The actual weight of the float is balanced by a sliding weight. The vertical movements of the float are recorded on the chart by the pivoted arm, which works through a gland.

This instrument, though rather outside the range of metering in the ordinary sense, is the most important one in the process of multiseparation as being a direct indicator of the efficiency of extra gasoline retention.

In the course of solubility experiments in 1926 the author noted and recorded that the specific gravity of crude which had been reduced to atmospheric pressure by slowly bleeding off gas from a 1500# well-head sample was appreciably less than that of the crude normally being produced on the field in question. The commercial significance of this phenomenon was not, however, appreciated at the time and it was not until 1929, as a result of Messrs. Gibson's and May's investigations referred to earlier, that multistage separation was recognized to be a practical oilfield process of gasoline recovery, being adopted on the Haft Kel field in 1930.

Independently in the States, Lindsley,[10] also working on well-head pressure samples in connection with solubility experiments, had obtained similar results, the specific gravity of his samples, after gradual evolution of gas content to atmospheric pressure, being appreciably less than that normally obtained by operators on the Kettleman Hills, Ventura Avenue and Oklahoma City fields.

References.

[1] Anon., *World Petrol.*, 1937, Feb., p. 67.
[2] E. O. Bennett, *Petr. Eng.*, 1936, Feb., p. 135.
[3] E. O. Bennett and C. R. Williams, *Oil & Gas J.*, 1937, May 20th, p. 55.
[4] E. S. L. Beale, *Science of Petr.*, 1938, **1**, 688.
[5] E. S. L. Beale, *J. Inst. Petr. Tech.*, 1937, **23**, No. 161, 213.
[6] E. Clark and F. A. Flinn, *Oil Weekly*, 1937, Feb. 22nd, p. 67.
[7] Amer. Gas. Assoc. (Nat. Gas Dept.), 1935, Gas Measurement Committee Report No. 2, Appendices B and C.
[8] L. A. Pym, *Proc. World Petr. Congr.*, 1933, **1**, 452.
[9] C. J. May, *ibid.*, 1937, Section I.
[10] B. E. Lindsley, *Trans. A.I.M.M.E.*, 1931, Petr. Divn., p. 252.

DISCUSSION ON METERING.

THE One Hundred and Seventy-ninth General Meeting of the Institution of Petroleum Technologists was held at the House of the Royal Society of Arts, John Street, Adelphi, W.C. 2, on Tuesday, January 11th, 1938, at 5.30 p.m. The Chair was occupied by the President, LT.-COLONEL S. J. M. AULD, O.B.E., M.C., D.Sc.

THE PRESIDENT said that the two papers to be presented that evening dealt with closely related subjects, and he hoped that a general discussion would follow on applied instrumentation in the oil industry. He had had the privilege of working with both the authors, and he did not know any two men more fitted to deal with the different aspects of the subject chosen.

The following papers were then presented :—

"The Application of Automatic Control to Refinery Process Operations," by S. W. Adey, B.Sc. (*See* p. 125.)

"Some Applications of Metering in Oilfield Operations," by Captain D. Comins, M.C. (*See* p. 140.)

DISCUSSION.

THE PRESIDENT said that the very important subjects dealt with by the authors had received scant attention in the general literature of the industry, although there was a wealth of information in the specialist literature of the manufacturers. He hoped that the designers and manufacturers of the equipment would take part in the discussion, and that they would stress the point which had been made in both the papers, *i.e.* the need for collaboration with the manufacturers prior to the apparatus being put into use and even before it was constructed.

DR. A. IVANOFF said : The two papers read this evening are of considerable moment, as they represent the problems of metering and automatic control as seen by the user. The authors have earned our thanks for making their papers very readable as well.

I find myself in general agreement with most of the ideas put forward, and, not wishing to criticize minor points, I should like to make my contribution an expansion of that part of Mr. Adey's paper which refers to the time lag in the plant under automatic regulation. To avoid complications of interest only to the specialist, the argument will be more popular than accurate.

Imagine a pressure vessel *A* (see Fig. 1) acting as a reservoir in a gas line. The pressure in the vessel is regulated by a valve on the inlet, and is indicated by a pressure gauge.

The smaller vessels, *B* and *C*, are connected to vessel *A* in the manner shown, and are also provided with pressure gauges.

The graph below (see Fig. 2) shows the course of the pressure change in each vessel following a sudden variation in the opening of the valve. In constructing the graph it was assumed that the pressure in each vessel was perfectly steady until the instant when the opening of the valve

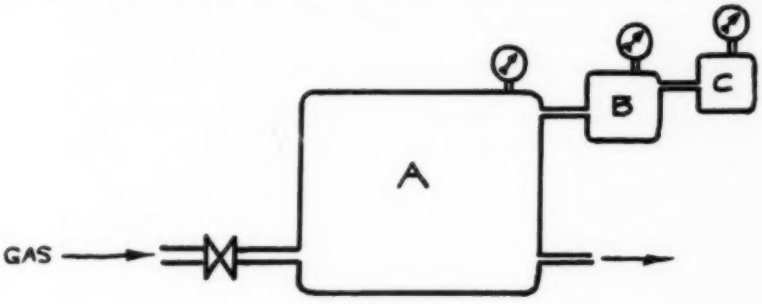

FIG. 1.

was increased sharply. The consequent pressure variation in the vessels *A*, *B* and *C* is given by the lines *Pa*, *Pb* and *Pc* respectively.

The difference between the shapes of the three curves and the shape of the curve of the valve opening is attributed to what is known as "time lag." Without going into the theory of the subject, it is evident that the character of the curves *Pb* and *Pc* differs materially from that of the

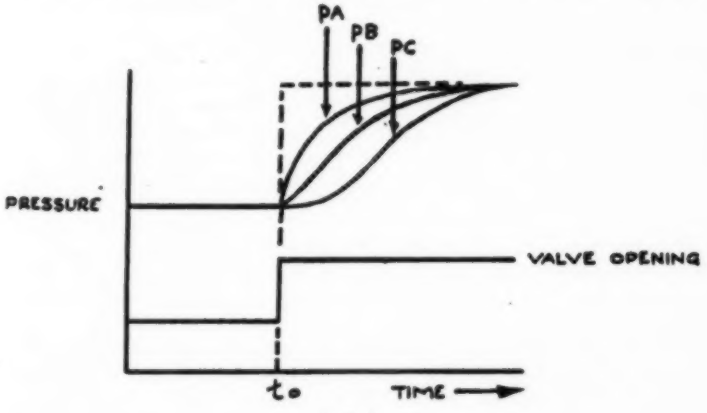

FIG. 2.

curve *Pa*. It is convenient to define the lag giving a curve such as *Pa* as a *single-stage lag*. Then the lag in the curve *Pb* is a *two-stage lag*, the two stages being from the supply line to *A* and from *A* to *B*. Similarly, the curve *Pc* exhibits a *three-stage lag*.

If the inlet valve were to be actuated by an automatic controller measuring the pressure in the vessel *A* and working on the proportional principle,

in the absence of any further lag in the control mechanism, the regulation would be dead beat, however high one made the sensitivity of the controller.

If the same controller were connected to the vessel *B*, the regulation would in the worst case be of a damped oscillation kind. By connecting the controller to the vessel *C* one would obtain stable control provided the sensitivity did not exceed a value of the order of 8. The exact value depends on the proportions of the vessels, resistance of connecting pipes, etc.

To give an idea of what is meant by a sensitivity of 8, a graph (see Fig. 3) was prepared showing the effect of a change of conditions on the pressure maintained by the controller. It was assumed that until the instant t_1 the conditions were steady. At the moment t_1 a disturbance occurred which, were the controller out of action, would have raised the pressure to the line shown dotted. By shutting the control valve partly the controller kept the pressure change down to a certain value shown as *deviation*. The difference between the disturbance and the deviation is the *correction* applied. Then the sensitivity is the ratio correction : deviation.

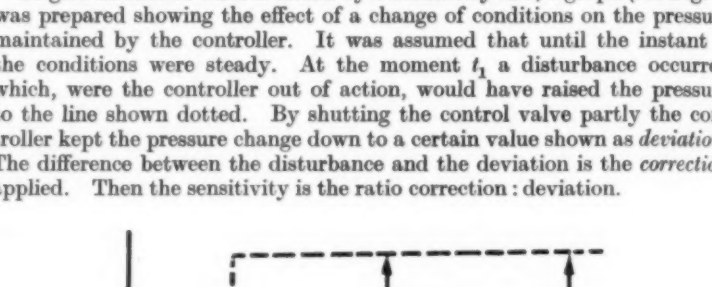

FIG. 3.

Pressure vessels are not often connected in the manner shown, but many of the installations amount to such a combination, especially if it is remembered that the head of a diaphragm valve can often be regarded as the last vessel *C*.

Many of the adverse combinations of plant and control equipment are much more difficult to analyse and to understand, and if automatic control is to be successful, one must plead for close co-operation between the designers of the plant and of the instruments. For preference, that co-operation should go as far as to allow the poor instrument man a little time in which to consider the problem before sending in the quotation.

MR. B. DUNGLINSON congratulated Mr. Adey and Captain Comins on their excellent papers and said that the subject with which they dealt was a highly specialized one of recent development. With regard to the theory of it, an excellent symposium had been delivered before the

Chemical Engineering Group * some time last year, and was available to anyone who cared to buy it.

He had been interested to hear Mr. Adey's comments on the misuse of the excellent temperature recorder. Twenty-three or twenty-four years ago he had been associated with the first cracking plant in this country, and that plant could not have been operated without pyrometers; there had to be one pyrometer on each still unit.

It occurred to him that the technique of refinery development must be associated with the technique of instrument development. He thought he was right in saying that the large continuous units could not possibly be run to-day without some form of automatic control. Mr. Adey had given some very interesting information about the economics of controls, and he thought such information would be very useful if it could be obtained for other industries. Unfortunately, the greatest development in automatic control had been in the oilfield; it was most difficult to get people in this country interested in such devices. If the time came when one could run a plant automatically with one operator only, there would be a great saving of labour, and possibly the products would have a definitely standardized physical or chemical characteristic. The labour problem had to be contended with in this country, and if one wanted automatic control, the question was invariably asked: "Is it going to save labour costs?" The subject was a very difficult one, being tied up with trade union regulations and things like that, and one could only argue on the economic basis that there would be increased efficiency. Sometimes that was a very difficult thing to justify, because of the fact that plants were working on base load lines, and this refers particularly to base load power stations associated with the electrical grid system.

Captain Comins had touched on the question of accuracy of flow metering as against tank metering, the differences being of the order of a quarter of 1 per cent. He would be very interested to know how the readings were obtained on the flow meter. Was an integrating flow meter used, giving direct reading in gallons or pounds, or was a recording flow meter used in conjunction with a planimeter?

Captain Comins said the details were given in an article by the chief mechanical engineer of the company in question. The article had been published last February.

Mr. E. S. L. Beale, referring to Mr. Adey's statement that it would be very much better to have one man only in charge of a plant in the case of an emergency, asked whether Mr. Adey thought it would be a good arrangement on a large plant to have all the necessary controls centralized on a panel in the control-house, so that they could be literally operated by one man. Remote control valves could be obtained nowadays, by which a wheel was turned in one place and a corresponding wheel such as that of a valve was turned by exactly the same amount at any distance. If one man had control over the whole blowing-down operation, and had the controls arranged in such a way, it might possibly be better than the present

* Conference of the Chemical Engineering Group, held at University College, London, on October 15th, 1937.

arrangement, in which there were several people running about to get all the things done in the proper order. It was quite possible that some such method might be developed without difficulty.

With regard to the accuracy of orifice metering to which Captain Comins referred, he thought that the only case in which reasonably accurate orifice metering was obtained was where the rate of flow was nearly constant, and that was largely the case, he believed, in oil-refinery work. When it was not constant, all kinds of difficulties arose, not only that of using a planimeter accurately on a chart with wide fluctuations of differential pressure, but often also that of making proper allowance for the change in Reynolds number in the orifice, etc. With a constant rate of flow of a single product and over a long period of time, he thought that very accurate orifice metering could be obtained if proper precautions were taken.

On the motion of the PRESIDENT, a hearty vote of thanks was accorded to Mr. Adey and Captain Comins for their papers and also to those who had taken part in the discussion, and the meeting then terminated.

MR. J. R. RATCLIFF wrote as follows: Mr. S. W. Adey's paper strikes me as a very restrained and well-balanced consideration of the advantages and disadvantages of automatic control; the rather elementary nature of the first section I do not consider any drawback, for, as the author says, a detailed description of each type is easily available from manufacturers when required.

The author has mentioned the possibility of air transmission of records to the panel, and while I agree that from a safety point of view it is preferable to having any sort of oil, even sealing oil, inside the control room, I do consider that any scheme of transmission replacing two differential connections by one impulse connection should be demonstrated over a long period of time before it is generally adopted, and that in all cases of distant transmission some form of mechanical indicator should be provided at the transmitting end so as to obtain the most direct check possible in cases where the accuracy is questioned. Electrical systems of transmission can either be made intrinsically safe so as to be incapable of passing dangerous currents or creating any dangerous sparks, or else made completely flameproof according to mining standards.

The author has pointed to the advantages of complete centralization, but I suggest that the urge for centralizing all instruments has now passed its zenith, and that with the number of instruments at present employed it is preferable to remove from the main operating panel those dials which have only a local importance, *e.g.* the meters measuring the gas to different zones of a furnace should, I suggest, be of the simplest type, and placed on or near the firing front, the operator having control over the total gas to burners for the purposes of plant operation and emergency shut-down.

One example illustrating the danger of over-centralization is given by a recent photograph of Captain Eyston's racing car, in which four of the seventeen indicator dials had to be covered to avoid confusion to the driver.

Meters for accounting purposes certainly need not be placed on the control room panel, and in many cases I suggest that the automatic con-

trollers should not be on the panel either, but that the controller should be placed close to its work, and should be non-recording, while the control room includes a simple recorder and the operators over-riding remote control.

In the first place, automatic controllers need more frequent attention from the maintenance men than do plain recorders, and if the controller and the flow or pressure record are incorporated in one instrument, the operator has nothing left by which to handle his remote control when the controller is being serviced.

In the second place, flow controllers particularly have frequently to be damped in order to obtain perfectly steady control, and this damping may with some types be so much that it takes a considerable time to equalize them for checking the zero. A plain undamped recorder to effect really accurate metering would not only allow the flow controller to be damped to its best advantage without regard to time of equalizing, but would also provide a permanently available record for the operator.

The same argument applies to non-recording pressure controllers used outside with pressure recorders or pressure gauges in the control room, but it will be noticed that I have not suggested the separating of record and control in the case of temperature. The first reason is that a non-recording temperature controller would have to be nearly as expensive as a recording instrument, and the second is that it is usual practice nowadays to have separate checking indicators which give the operator independent indication.

A third reason is that temperature controllers are not damped, as pressure and flow controllers frequently are, and a fourth that it is more frequently possible to service the control portion of a temperature controller without disturbing the record.

With regard to the economy to be expected from an installation of automatic control, it seems to me that the author is too pessimistic in his installation estimate; I am not forgetting that the paper refers only to refinery practice, but manufacturers are expected to install controllers in general industrial work for 10 per cent. of this figure. However, as I think that his overall maintenance cost is unduly optimistic (bearing in mind the nature of most present-day controllers), his figure is not very different from the figure I should obtain—namely, £27 per annum.

I suspect rather that in arriving at the overall maintenance costs the author has considered the instruments only, whereas automatic-control installations naturally call for manual distance control in addition, and therefore, when considering a complete installation, an overall comparison should be made between the old type of plant with simple valves, simple instruments and larger staff, and the modern plant with all the implied accessories.

Mr. E. S. L. Beale, in a written contribution, said that in connection with the accuracy of metering and measurement of oil generally, there is one systematic error, the importance of which is quite often ignored, and that is the very large change in the specific gravity correction factor for most waxy oils at temperatures below about 100° F., and in some cases as high as 140° F. This point is mentioned in one of the papers referred to by Captain Comins.

The use of the usual specific gravity correction factors or volume correction tables, such as those of the well-known Bureau of Standards Circular 154 and others, may introduce a very considerable systematic error when the specific gravity or the volume of a waxy oil is converted from a relatively high temperature of measurement, such as 100° F. or above, to the usual reference temperature of 60° F. This may in itself cause an error of over ½ per cent., quite apart from any error due to the use of the wrong correction for the wax-free oil, such as may easily be produced by the use of the "abridged" form of volume correction tables which are essentially inaccurate. This may cause a further error of as much as ½ per cent.

These particular errors are both avoided by measuring the specific gravity of the oil at or near to the temperature of the tank, or the temperature of flow in the case of orifice meters, and then calculating the tonnage directly from these measurements, instead of attempting to correct either the volume or the specific gravity to 60° F. or expressing the results by volume at 60° F. instead of by weight.

Dr. F. V. A. E. Engel, in a written contribution, observed that Captain Comins' paper raised several important points which refer, in particular, to the accuracy of measurement of oil flow.

Captain Comins gives the accuracy of tank measurements to be within ± 0·25 per cent., which corresponds to the value given in British Standard Specification * No. 599/1935. From the practical point of view, it is obvious that the orifice method is preferable, provided that it leads to a similar standard of accuracy.

The author mentions results by the A.G.A. Committee giving the tolerance of discharge coefficients for orifice plates as ± 0·5 per cent. Recently the writer † compared the discharge coefficient as recommended in the V.D.I. Standards ‡ with results obtained by S. R. Beitler (U.S.A., 1935) and M. Marchetti (Italy, 1936). Comparison of the various coefficients gave very satisfactory results, being close to the above-mentioned accuracy.

A high degree of accuracy is, however, related to a certain limiting Reynolds number, which depends on the area ratio of the orifice; *e.g.* in the case of an area ratio of 0·4, the limiting Reynolds number referring to the pipe diameter is 125,000. Above this limiting Reynolds number the discharge coefficient may, from a practical point of view, be considered as a constant for a given area ratio. For flow conditions relating to Reynolds numbers below this limiting value, the coefficient becomes variable. The amount of variation increases considerably with increasing area ratios.

For oil measurement, working normally over a range of comparatively low Reynolds numbers, small area ratios and great differential pressures are therefore preferable. Difficulties may result from this in the case of crude oil measurement, especially if free gas is present. It would be of particular interest if Captain Comins would present some typical data on orifice calibration tests with crude oil in the conclusion of the discussion,

* B.S.S. for Pump Tests, No. 599/1935, London, March 1935.

† F. V. A. E. Engel and J. W. E. French, "Orifices for Flow Measurement," *Engineering*, 1936, **142**, 410–412, 496 and 497.

‡ "Regeln fuer die Durchflussmessung mit genormten Duesen und Blenden." V.D.I. Durchflussmessregeln DIN 1952. 4th Edition, Berlin, 1937.

giving also some data encountered in practice of pipe sizes, viscosity, static pressure before the orifice plate, area ratio and maximum differential pressure across the orifice for crude oil measurement.

The writer is of the opinion that considerable errors may arise due to the expansion of the free gas in the " vena contracta " on the downstream side of the orifice plate. This may influence the results to the same extent, even if the tapping points are arranged adjacent to the faces of the orifice plate.

Altogether, the orifice method has great possibilities in the field of oil-flow measurement, and it is to be expected that it will be more widely applied in this direction.

In this connection it may be of interest to mention that for the first time, as far as the writer is aware, the orifice method has been accepted (in Germany) as of sufficient accuracy to warrant orifice gas meters being certified just as the ordinary type meter.* This will certainly give a great stimulation to the application of the orifice method, and it is to be assumed that in the near future certificates will also be issued for orifices metering other media.

In conclusion, the writer would like to ask the author to give an explanation of certain terms used which do not seem to be in line with those generally applied in hydrodynamics and aerodynamics. Terms like " static pressure," " pressure head," " velocity head," etc., have certain meanings, and the reader of Captain Comins' paper may have some difficulty when terms like " flowing pressure " and " flow-head pressure " occur, especially as they seem to be applied to different conditions. " Flowing pressure " is mentioned once in connection with Pitot tube measurement, and in another section it seems to refer to a static pressure measurement. A term like " flowing pressure " may easily be mis-interpreted as a value corresponding to a velocity pressure or velocity head.

Mr. H. Hyams wrote as follows : In connection with the section dealing with comparative accuracy of metering and tank dips in Captain Comins' paper, I desire to submit the following observations :

Whilst it may be true to say that metering is largely carried out by the major oil companies at their producing fields, where a high degree of accuracy is not essential, the same statement cannot correctly be made to apply to refineries. Many refineries act as shipping centres for finished products, the accuracy demanded in the quantitative measurement of which is much greater than that necessary for movements of crude oil within the refinery. Because measurement by dipping can be more accurately carried out than measurement by metering, the former method is very widely used in those refineries where measurement of the crude has to tie up closely with measurement of the finished products despatched. The statement made by Captain Comins that the accuracy obtained by good metering is of the same order as that obtained by tank dipping, where the latter is *not* scientifically controlled, is an admission that measurement by dipping is superior to measurement by metering. Improvements in the process of tank dipping have been substantial in recent years. Tank

* *Reichsgesetzblatt*, Teil 1, Nr. 79 (July 10th, 1937), pp. 745–751.

calibration work can now be carried out to an accuracy of at least 0·05 per cent.; equipment such as dip tapes, weights, sampling apparatus, water-finding materials, thermometers and hydrometers are purchased by the large oil companies to standard, stringent specifications. It can therefore be said that in the vast majority of instances tank dipping is, in these days, to use Captain Comins' words, "scientifically controlled."

Captain Comins' reference to the determination of the average specific gravity of the contents of a tank and the correction of volume of oil from tank temperature to a standard temperature confuses the issue. The comparison between tank dipping and metering is solely on the basis of absolute volume. The question is whether one can get an absolute volume more accurately by dipping a tank than by using a meter. Specific gravity does not come into the picture; if correction to standard temperature is required, a volume coefficient has to be applied both to volumes obtained by tank dipping and by metering.

There are admittedly difficulties in securing the correct average temperature of the contents of a large storage tank, but I submit that these difficulties are no greater than those associated with the determination of the average temperature of a quantity of oil which is flowing through a line and passing through an orifice meter.

Later on in his paper, Captain Comins submits that an accuracy of $\pm$ 1 per cent. for metering, with all precautions taken, is a reasonable figure. With this I agree, but I do not agree with his other figure of $\pm \frac{1}{4}$ per cent. for tank dipping under precise scientific control. If oil companies could not guarantee their measurements by tank dipping to a greater accuracy than $\pm \frac{1}{4}$ per cent. they would be inundated with complaints from customers who purchase large quantities of oil under contract. $\pm \frac{1}{10}$ per cent. more closely approaches the accuracy which is nowadays obtained by the dipping method, and even this has been very largely improved upon at larger refineries and installations, where repeat dip readings can be obtained to within 1–2 millimetres.

I also do not agree with Captain Comins' contention that tonnage quantities rather than volumetric figures are the rule for fiscal and sales purposes. Efforts have been made through the I.P.T. and through the First World Petroleum Congress to secure universal measurement on a volumetric basis and, although great progress has admittedly not been made in this direction, there is, on the other hand, no observed tendency for Customs and other authorities to change over from the volume to the weight basis.

It is not possible to enter into a discussion here on the merits or disadvantages of the mercury gauge which indicates the weight of a volume of oil in a storage tank. I suggest that such a gauge has definite limitations, requires very careful control if a reasonable degree of accuracy is to be maintained and that only under very special conditions would the cost of its installation and maintenance provide any economy over the more established method of tank dipping.

The quotation from the report of the Mexican Eagle Co. is not, in my opinion, very convincing. A difference of $\frac{1}{4}$ per cent. over the year's working may or may not be of great importance in balancing stocks of crude oil in the field. If we were to assume that in a certain instance tank dip-

ping gave very accurate figures, whilst metering gave figures ¼ per cent. too high, this might involve the producing company in a considerable sum of money per annum in the payment of royalties to the local government. The statement made in the Mexican report, "It is, in fact, generally considered that any error more probably lies in the tank gauging," should, in my opinion, be backed by evidence. If this observation can be proved, my experience leads me to say that the tank dipping cannot have been carried out under the scientific control that is really necessary.

Towards the end of this section it is said that differences between metering and tank dipping are usually of the order of 1 or 1½ per cent. These comparisons tend to be misleading. One should determine the absolute accuracy of each method before making comparisons. If one were to assume that tank dipping gave an error of $-\frac{1}{10}$ per cent., whereas metering, over a period, showed an error of $+\frac{9}{10}$ per cent., we should have a difference of 1 per cent. between dipping and metering, but the individual absolute figures would give us the true picture of the accuracy obtainable by each method.

Paragraph (*e*) of this section, in my opinion, sums up the situation regarding the accuracy obtainable by metering. Even when orifice plates are accurately designed and carefully made, an error of $\pm \frac{1}{2}$ per cent. is possible under this head only. When one adds to this the other possible errors referred to by the American Gas Association and the increase in error resulting from wear of the meter in the course of time, one gets a true picture of the limited accuracy of flow meters, and how poorly they compare with the dipping method for measurement of volume quantities of liquids.

CAPT. D. COMINS, replying to the Discussion, wrote as follows: Two points made by Dr. Engel—the first concerning errors due to expansion of free gas on the downstream side of an orifice plate, and the second concerning the meaning of certain terms used—will be replied to in detail, as these concern the body of the paper, the metering of "live" crude.

The introductory section, raising for discussion the question of the relative accuracy of metering as compared with tank dips, appears, however, to have aroused more interest—perhaps one should say controversy—the remainder of the discussion being around this question.

The only "live" crude metering operation, described in the paper, in which there is definitely free gas present to expand in the "vena contracta" on the downstream side of the orifice plate, is in the measurement of production by the portable tank and gas bags method. Here, however, as explained in the text, the orifice meter is not itself used for measuring the well's rate of production, this being measured in the portable tank. The differential pressure recorded at the orifice meter provides a means of setting the tank valve accurately in all tests "in order to ensure that flow when diverted to the tank is at the same rate as when flowing in the line"; and, in successive tests at lower rates than full flow, of setting the production valve at the well in order to ensure that the rate of production is roughly in the proportion of full flow desired for each test.

In the case of metering "live" crude at well-head separators, the meters are installed close to the separators on the outlet side in order to ensure that there shall be no free gas present at the pressure of measurement.

The assumption is, of course, involved that separation has been fully effected, this representing a possible source of error, not merely on account of the expansion of the gas in the "vena contracta," but in the basic calculation of flow. As mentioned, however, in the text, metering at well-head separators is only carried out as a means of allocating to individual wells the communal total production of several wells metered after the last stage of gas separation. The latter being the basic production figure in all oilfield operations, errors in the allocation of this figure over individual wells are comparatively unimportant.

In pumping multistaged crude through main pipe lines, the line pressure is maintained high enough to prevent evolution of gas.

Dr. Engel suggests that certain terms used in the paper require definition. I would point out that familiarity with the ordinary terminology of production operations was presumed and, on re-reading the text, the only term I can find of purely local coinage is "Datum Pressure," which is the pressure in the reservoir at a fixed elevation, known as "Datum Level." Various other terms either have no application or are not used in hydrodynamics or aerodynamics, for example :—

"*Reservoir Saturation Pressure*"—the pressure at which gas first begins to be evolved from solution from reservoir crude at reservoir temperature. (Reference Paper by the author to World Petroleum Congress 1933.)

"*Bottom Hole Static Pressure*"—the pressure of the reservoir crude at the main producing show of a well, after static equilibrium has been reached with the well shut in.

"*Bottom Hole Flowing Pressure*"—ditto whilst flowing at any given rate of crude production.

"*Bottom Hole Differential Pressure*"—the difference between Bottom Hole Static Pressure and Bottom Hole Flowing Pressure.

"*Static Pressure*" (of an oil well)—the oil pressure at a point of known elevation at the Flowhead, after all free gas evolved from solution from the crude has been bled off and static equilibrium has been reached.

"*Flowhead Pressure*"—a general term to cover cases, as *e.g.* in Figs. 9 and 10, where the reference may be to either the Static Pressure or the Flowing Pressure of a well.

Having regard to their context, no oilfield operator would misinterpret the meaning of the general terms flowhead pressure, flowing pressure, line pressure, and static pressure, used for convenience throughout the text. In referring to the Pitot Tube measurement, the flowing (or line) pressure measured at the static, as opposed to the Pitot Tube, connection was for clearness referred to as the static pressure. In all other cases it was taken for granted that it would be understood that the term "flowing pressure" refers to pressure head only.

Coming now to the discussion of accuracy of metering and of tank dips, I would observe that, although this is of great value, as coming from recognized authorities on the subject, it is disappointing to find that no data or facts are quoted regarding the attitude of specific companies or countries in this matter. The point was raised in the hope of provoking

such information, and the tentative deductions drawn in the paper did not claim to be more authoritative than was justified on the rather limited information quoted.

The point made by Dr. Engel regarding the relation of accuracy to Reynolds number is fully appreciated, but in most cases the value of this criterion can be kept high enough to avoid risk of inaccuracy, especially with Iranian crudes, which have low viscosity. Mr. Adey, in the companion paper to this, refers to the difficulty of metering at very low Reynolds numbers, *i.e.* in the viscous region.

Mr. Hyams' contribution emphasizes the controversial nature of this question and the desirability of ventilation. In contrast to Dr. Engel, who agrees with the orders of accuracy suggested in the paper, Mr. Hyams' experience is that there is a greater divergence between metering and tank dip figures, but he stresses comparison on a volumetric rather than a weight basis. Whether this is admissible depends, of course, on individual circumstances, and it is to be regretted that he does not quote specific cases of large organisations whose sales are on a volumetric basis, as this is essentially a matter of fact rather than of opinion.

In this connection it may be remarked that it is difficult to draw up satisfactory internal refinery balance sheets except on a weight basis, as, for striking a balance conveniently, the amounts of gas evolved in process have to be accounted for in the same units as the crude.

On a weight basis, Mr. Hyams' view may not be generally accepted that the average specific gravity and temperature of the contents of a tank can be determined as accurately, for purposes of conversion from volume to weight, as the average specific gravity and temperature in a line, where the exact temperature can be continuously recorded and representative samples continuously by-passed and slumped for specific gravity determination. This is, however, a matter of experience and investigation and Mr. Hyams' view must, therefore, carry considerable weight.

Mr. Hyams also contends that tank dips, rather than metering, are widely used for internal purposes in refineries as well as for measurement of finished products shipped. This may very well be preferable in small refineries, or even in larger ones handling a number of crudes of basically different characteristics. In really large refineries, however, handling one type of crude, the cost of basing internal figures on tank dips is, owing to the amount of extra tankage required, so much greater than the cost of metering that it may only be justified on economic grounds for very special reasons.

Mr. Beale's contribution on the difficulty of converting volume figures for waxy oils into weight figures at temperatures remote from that of specific gravity determination, being a question of fact, calls for no comment, but is, none the less, highly relevant.

CALIBRATION OF I.P.T. DIESEL REFERENCE FUELS H.I.Q. AND L.I.Q. IN TERMS OF CETANE AND CETENE NUMBERS.

Introduction.

Secondary reference fuels are to be preferred to primary standards in the routine testing of diesel fuels for ignition quality for two reasons. Firstly, the high cost of primary standards makes it impracticable to use them except for purposes of calibration. Secondly, the use of primary standards such as cetene, cetane and α-methylnaphthalene involve additional experimental error, since they are not typical of normal fuels in regard to specific gravity, viscosity, etc., and under some conditions of engine operation lead to peculiarities in the timing and manner of opening of the fuel valve.

It was the opinion of the I.P.T. Diesel Panel that the adoption of common secondary reference fuels would lead to a closer agreement of results between laboratories, and it was decided that the Anglo-Iranian Oil Company, Ltd., should be asked to manufacture suitable reference fuels, which would be designated I.P.T. High-Ignition-Quality Reference Fuel and I.P.T. Low-Ignition-Quality Reference Fuel. These reference fuels are now available for general use.

The calibration of the I.P.T. secondary reference fuels, in terms of cetane and cetene numbers, was undertaken on behalf of the I.P.T. Diesel Panel by the following laboratories :—

Proefstation Delft (Bataafsche Petroleum Maatschappij).
Vauxhall (Esso European Laboratories).
Sunbury (Anglo-Iranian Oil Co., Ltd.).

All tests were made by the Ignition Delay Method (I.P.T. Method 1), but the engines and operating conditions varied for the different laboratories, as is indicated below :—

Engines and Operating Conditions.

Laboratory A.

(*a*) Thomassen engine : 275 r.p.m., 20 lb./sq. in. B.M.E.P., jacket temperature 50° C.

(*b*) Gardner engine : 1000 r.p.m., 69 lb./sq. in. B.M.E.P., jacket temperature 70° C., injection 13° before T.D.C.

(*c*) Ricardo engine : 1100 r.p.m., 32 lb./sq. in. B.M.E.P., jacket temperature 60° C., injection 19° before T.D.C.

Laboratory B.

(*a*) Gardner engine : 1000 r.p.m., 70 lb./sq. in. B.M.E.P., jacket temperature 45° C., injection 17° before T.D.C.

(*b*) C.F.R. engine (turbulent head): 900 r.p.m., 13 c.c. consumption of fuel/minute, jacket temperature 100° C., air intake temperature 65° C., injection 10° before T.D.C., compression ratio adjusted to give a constant delay of 10°.

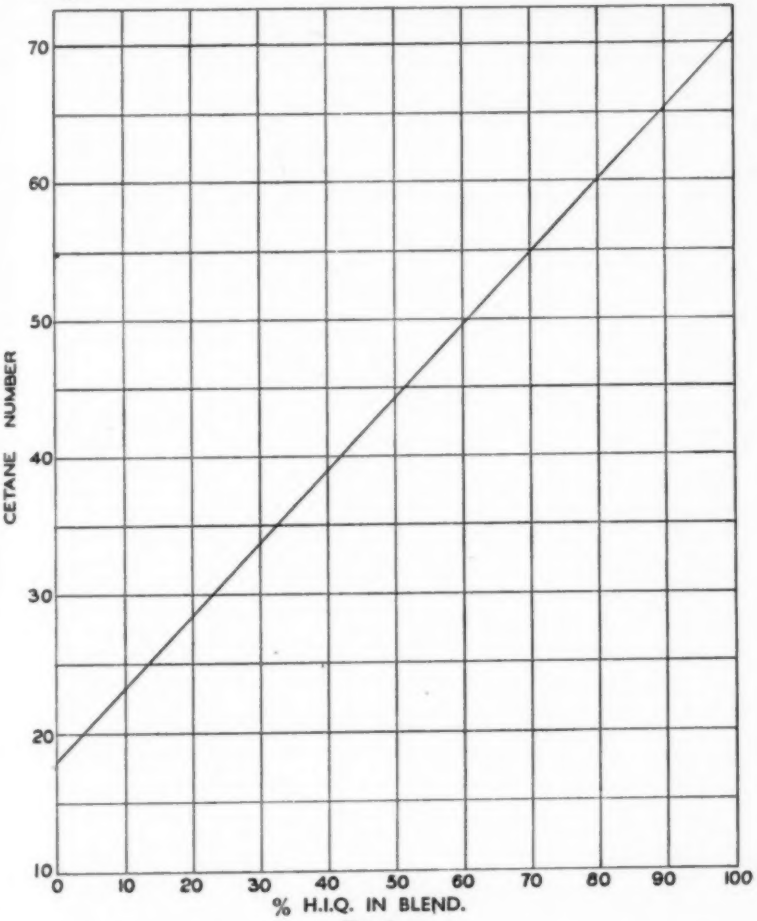

FIG. 1.

CALIBRATION OF I.P.T. DIESEL REFERENCE FUELS (BATCH 1). *Sept. 1937.*

These conditions are almost identical with those recommended by the S.A.E. Volunteer Group for C.I. Fuel Research * in their "Tentative Standard Operating Conditions and Procedure for Delay Period Method of Rating Diesel Fuels."

* Now known as the Automotive Diesel Fuels Section of the Co-operative Fuel Research Committee.

Laboratory C.

(*a*) Gardner engine: 1000 r.p.m., 70 lb./sq. in. B.M.E.P., jacket temperature 70° C., injection 17° before T.D.C.

(*b*) C.F.R. engine (turbulent head): 900 r.p.m., 13 c.c. consumption

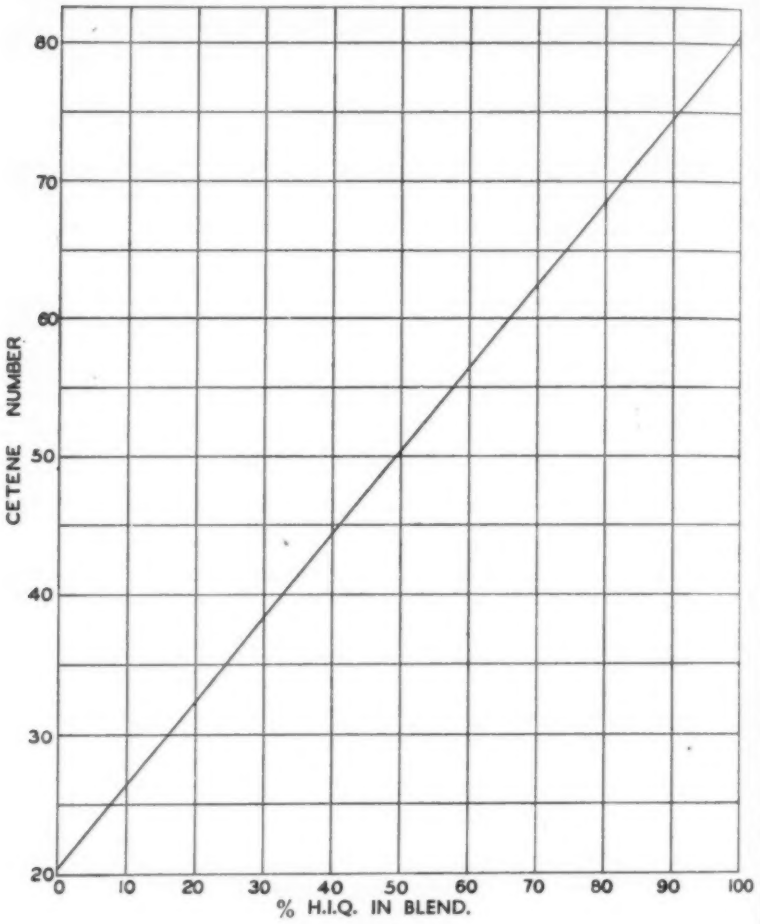

FIG. 2.

CALIBRATION OF I.P.T. DIESEL REFERENCE FUELS (BATCH 1). *Sept. 1937.*

of fuel/minute, jacket temperature 100° C., injection 10° before T.D.C., compression ratio 13 : 1 for fuels above 45 cetane number and 16 : 1 for fuels below 45 cetane number.

Where no air intake temperature is indicated, no heating was applied.

Primary Reference Fuels.

The official cetane and α-methylnaphthalene were obtained from the Dupont Company, but check tests were also made on materials obtained from several other sources. As the results were in reasonably close agreement, it may be concluded that the primary standards can be manufactured to a sufficiently close specification.

The cetene used was manufactured in the Shell Amsterdam Laboratory.

Methods of Indicating the Delay Angle.

Laboratory A.

Thomassen engine : Piston indicator.
Gardner engine and Ricardo engine : Optical indicator.

Laboratory B.

Cathode-ray oscillograph indicator.

Laboratory C.

Cathode-ray oscillograph indicator.

Summary of Results.

The tables below give the individual results obtained by the co-operating laboratories, together with averaged values :—

Cetane Correlation.

Blend % H.I.Q.	Laboratory A.				Laboratory B.			Laboratory C.			Mean of all Labs.
	Thomassen.	Gardner.	Ricardo.	Mean.	Gardner.	C.F.R.	Mean.	Gardner.	C.F.R.	Mean.	
100	73	73	75	73½	70	69	69½	68½	68½	68½	70½
90	66	66½	68	67	65	64½	65	64½	64½	64½	65½
80	59	60½	62½	60½	60	59½	60	60	60	60	60
70	53	54½	56½	54½	55	54½	55	55	55	55	55
60	47½	49½	51	49½	50	49½	50	50	50	50	50
50	42½	44½	45	44	45	44	44½	44½	44½	44½	44
40	37½	40	40	39	40	38½	39	39	39	39	39
30	32½	35½	35	34½	35	33	34	32½	32½	32½	33½
20	28	31½	30½	30	30	27½	29	26	26	26	28½

Cetene Correlation.

Blend % H.I.Q.	Laboratory A.				Laboratory C.			Mean of Lab. A and Lab. C.
	Thomassen.	Gardner.	Ricardo.	Mean.	Gardner.	C.F.R.	Mean.	
100	80	82½	88	83½	78	78	78	80½
90	72½	75½	81	76½	73½	73½	73½	75
80	66	68½	73½	69½	68½	68½	68½	69
70	59½	62	66½	62½	63	63	63	63
60	53½	56	59½	56½	57	57	57	57
50	48	50	52½	50	50½	50½	50½	50
40	42½	44	46	44½	44	44	44	44
30	37	38½	39	38	37	37	37	37½
20	32	33	32½	32½	29½	29½	29½	31

Discussion.

In spite of the large differences in the engines and test conditions, the results obtained agree very well with each other. Between 35 and 60 cetane number, which covers the range of fuels in commercial use, the agreement is well within the limits of experimental error on a given engine.

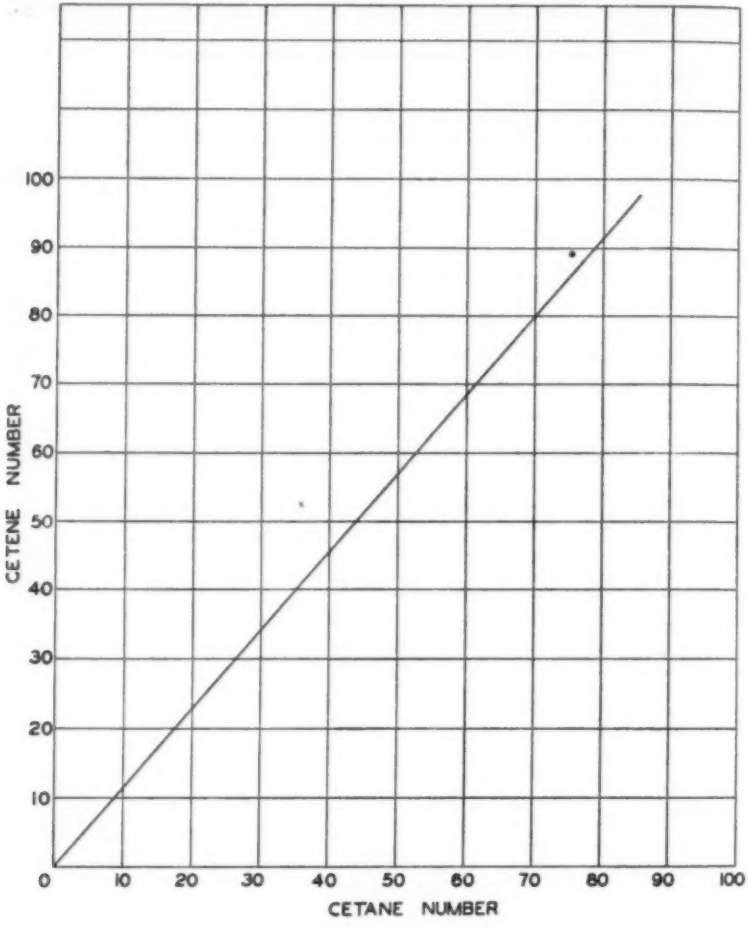

Fig. 3.

CALIBRATION OF I.P.T. DIESEL REFERENCE FUELS (BATCH 1). *Sept. 1937.*

The averaged values, when plotted, lie very close to the straight lines indicated in Figs. 1–3, and these mean calibrations have been agreed upon by the participating laboratories.

Conclusions.

(1) That the cetane number of H.I.Q. reference fuel is 70½ and L.I.Q. reference fuel 18, and that the calibration is a straight line.

(2) That the cetene number of H.I.Q. reference fuel is 80½ and L.I.Q. reference fuel 20½, and that the calibration is a straight line.

(3) That the cetane number–cetene number relationship is a straight line from the origin passing through the point 80 cetene number = 70 cetane number.

(4) That, on the basis of these tests, the maximum experimental error to be expected on a suitable test engine is ± 2 cetane numbers.

IGNITION QUALITY OF DIESEL FUELS.

THE ignition quality of a fuel is a measure of the relative time required for combustion to start after the commencement of injection : the shorter the time the higher the ignition quality.

High ignition quality indicates ease of starting and smoothness of running, but the ignition quality of a fuel is not necessarily an indication of its combustion quality in all types of compression ignition engines. Furthermore, hot-bulb engines have special requirements, as have engines which use spark ignition for heavy oils. No form of test is suitable for rating fuels for these engines except direct tests in the engines themselves.

The routine test described below involves the use of reference fuels calibrated by the I.P.T. Diesel Panel, but it should be mentioned that other suitable secondary reference fuels have been employed elsewhere.

Two methods of test have been described in I.P.T. Serial Designation F.O. 39(T). Method 1 is preferred for routine cetane number determinations, but Method 2 has the special advantage of being readily applicable to a large range of diesel-engine types, and is therefore convenient for making comparisons of fuel ignition quality where special apparatus is not available.

TENTATIVE METHOD OF DETERMINING IGNITION QUALITY OF DIESEL FUELS.*

I.P.T. SERIAL DESIGNATION F.O. 39(T).†

THIS method shall be used for the determination of the ignition quality of diesel fuels for compression ignition engines, with the exception of doped fuels.

The ignition quality is expressed as cetane number. The cetane number of a fuel is defined as, and is numerically equal to, the percentage, by volume, of cetane in a mixture of cetane and α-methylnaphthalene which has the same ignition quality as the fuel when compared by either procedure given below.

The ignition quality of a fuel is a measure of the relative time required for combustion to start after the commencement of injection; the shorter the time the higher is the ignition quality.

* This method supersedes the method previously issued and published in *J.I.P.T.* 1936, **22**, 774–778.

† The Diesel Fuel Panel of the Chemical Standardization Committee of the Institution of Petroleum Technologists hope that those concerned with the testing of diesel fuels will put forward any comments on the use of the method and of the secondary reference fuels in experimental work which would assist the Panel in their deliberations. Comments should be addressed to the Secretary, The Institution of Petroleum Technologists, Aldine House, Bedford Street, London, W.C.2.

The delay angle is the angle in degrees of crankshaft rotation which elapses between the commencement of injection and the beginning of discernible combustion, as determined by pressure rise from the compression line.

Under any given engine conditions the delay angle is a function of the ignition quality, which latter is independent of engine conditions or engine within the limits set forth below.

Delay angles in degrees of crankshaft rotation are affected by engine characteristics, running conditions, etc., and may vary for a given fuel over a wide range.

Reference Fuels.

(*a*) The primary reference fuels are cetane and α-methylnaphthalene.*

(*b*) Secondary reference fuels.

To ensure a greater degree of reproducibility in testing, the secondary reference fuels mentioned hereafter shall be used. These have been calibrated by the delay method against primary reference fuels on a number of engines by the I.P.T. Diesel Fuel Panel.

The secondary reference fuels are those designated as I.P.T. high-ignition-quality and I.P.T. low-ignition-quality secondary reference fuels.

The high-ignition-quality secondary reference fuel is a highly refined Iranian gas oil produced by sulphur dioxide treatment from straight-run gas oil (Batch No. 1 of this fuel has a cetane number of 70·5).

The low-ignition-quality secondary reference fuel is a refined sulphur dioxide extract from Iranian kerosine (Batch No. 1 of this fuel has a cetane number of 18).†

The cetane number of blends of these fuels is determined from a graph showing composition plotted against cetane number. The relation between composition of the secondary reference fuel blends and cetane number is a straight line between the points 70·5 cetane for 100 per cent. high-ignition-quality secondary reference fuel Batch No. 1, and 18 for 100 per cent. low-ignition-quality secondary reference fuel Batch No. 1. (*See Fig.* 1, page 171.)

Apparatus.

Type of Engine.

It has not been found necessary to standardize any particular engine for the determination of ignition quality. Any compression ignition engine with a high compression ratio can be used for Method 1, provided it can be adjusted to give constant spray valve opening time on all fuels, and provided that it has steady ignition characteristics. A four-stroke cycle engine of similar characteristics is required for Method 2.

Method 1.

An indicator is required with which a change of one-quarter of a degree of

* The question of suitable standards of purity for these hydrocarbons is being considered by the I.P.T. Diesel Fuel Panel.

† These fuels are obtainable from the Anglo-Iranian Oil Co., Ltd., Britannic House, Finsbury Circus, London, E.C.2.

crankshaft rotation is accurately measurable. The indicator should be suitable for determining, to the same accuracy, the angle at which lift of the spray valve occurs.

Method 2.

An expansion chamber of capacity at least ten times the piston displacement is required, and should be coupled to the induction pipe of the engine. The inlet to the expansion chamber should be fitted with coarse and fine control valves or their equivalent. A suitable vacuum gauge or manometer is required which will measure pressures from atmospheric to 63·5 cm. (25 in.) of mercury below atmospheric, and which will read to within 0·254 cm. (0·1 in.) of mercury. The vacuum gauge or manometer should be coupled to the expansion chamber and means provided to damp out pressure fluctuations so that a steady reading of pressure is obtained.

METHOD.

Method 1—*Ignition Delay Test.*

Operating Conditions.

For this test the engine should be run at normal speed or, in the case of variable-speed engines, at not less than one-half of the maximum speed. Load should be maintained constant, and may be any desired fraction of full load giving steady operation and clear exhaust.

The inlet air and water-jacket temperatures should be maintained constant to within $\pm$ 2° C. during the tests and at normal values for the engine used. The tests should not be commenced until these temperatures have become steady. The fuel spray valve should be free from carbon trumpets. The load and speed should not be such that erratic opening is liable to occur with any viscosity of fuel examined.

Outline of Procedure.

With the engine running under steady conditions as specified above, the delay angle is measured on the fuel to be tested. Individual readings should not differ by more than half a degree, and sufficient readings should be taken to give reproducibility on the averaged result at least to one-quarter degree of crankshaft angle.

Suitable blends of the secondary reference fuels are then chosen so as to bracket the fuel under test, and the delay angle of these blends is then measured. The relation between cetane number and delay angle is not linear, and sufficient blends of the secondary reference fuels must be taken to enable a curve to be plotted showing the relation between composition of the blends and delay angles. The proportion of secondary reference fuels in a blend to match the fuel under test shall be determined from this curve.

The delay angle/composition curve will change from day to day by small amounts, and a curve previously determined can only be used as a rough guide.

The cetane number will then be determined from the curve showing the relationship between cetane number and percentages of secondary reference fuel blends.

Method 2—Throttling Test.

Operating Conditions.

The engine should be run at normal speed, or at not less than half full speed for a variable-speed engine. The load should be maintained at one-eighth full load or at the lowest load above this which will give steady running; in no case should the operating load be greater than one-quarter full load.

The inlet air and water-jacket temperatures should be maintained constant to within $\pm 2°$ C. during the test and at the normal values for the engine used.

Outline of Procedure.

With the engine running under steady conditions as specified above, the fuel to be tested is introduced and the throttle valve steadily closed, keeping the speed constant. At a certain point the engine will start to misfire, which can be observed by a puff of white smoke from a test cock provided in the exhaust pipe. The pressure in the expansion chamber at which misfiring commences should be recorded, and at least two separate observations should be made and the average taken. Sufficient blends of the reference fuels should be tested in the same way to bracket the sample, and the equivalent blend of the reference fuels which gives the same critical suction pressure as the sample fuel can be obtained from a curve plotted from the determinations made on the reference fuels.

The cetane number is then determined from the secondary reference fuel matching blend as in Method 1.

Reproducibility.

The results obtained by either method for a given fuel on a suitable engine should not differ by more than ± 2 cetane numbers.

Method of Reporting Results.

Cetane number should be reported to the nearest even integer.

SLUDGE AND SLUDGE FORMATION IN CRACKED RESIDUES.*

By J. Voskuil and I. Robu.

Synopsis.

Several cracked residues from different base materials, and cracked under varying conditions, were microscopically examined. It was found that the microscopic images varied widely. Some were almost homogeneous even with dark ground illumination, like the straight-run residues, and others contained very many inhomogeneities (sludge). With the aid of a working hypothesis the origin and nature of this sludge are discussed. As it is in most cases impossible (owing, for instance, to viscosity) to determine directly the quantity of sludge in residues and in mixtures of residues with gas oil, an indirect method was evolved. This method consists in determining the quantities of precipitate formed in a residue with various quantities of a precipitant hydrocarbon (*e.g.* 60/80 gasoline, mixtures of gasoline and benzene). If the percentages of precipitate are plotted on a graph as a function of the quantity of precipitant hydrocarbon, and the resultant curve is extrapolated on the graph or with the aid of an empirical formula, to a dilution of the hydrocarbon of zero, the quantity of sludge in the residue is found.

The occurrence of heater sludge in the preheaters of oil burners when using cracked residues as fuel components is discussed. It was found that the conversion of sludge into heater sludge depends on the medium. If the medium contains too few materials that have a stabilizing effect on the sludge, the latter is converted into heater sludge. Oxygen plays an important part in this respect.

Introduction.

It is a well-known fact that residues from cracking processes may, in certain circumstances, show a tendency to liberate sludgy matter. The trouble brought about by this propensity has considerably diminished since the introduction of cracking to a lower specific gravity of the residue, but it is still a factor of sufficient importance to give the oil engineer cause for worry. The phenomenon—which may occur as a deposition of sludge or a gelatination of the residue, and which will be referred to as " sludge formation " from here on—can be brought about by a variety of influences, of which the most usually met with are time (storage), dilution (for instance, with a gas oil), and heating to a moderate temperature (*e.g.* 100° C.).

The literature on this subject may be divided into investigations dealing with :

(*a*) the chemical composition of the sludge,
(*b*) methods of determining sludge, and
(*c*) methods of preventing sludge formation in practice.

Chemical investigations on the composition of the sludge are in an initial stage, a fact which is undoubtedly due to the complex composition of the substance. Possibly the problem will be attacked more fundamentally if ever the sludge acquires commercial value.

* Paper received October 26th, 1937.

Sludge determinations which have been employed or proposed in the past have invariably been made with the aid of diluents or precipitants, and as these must necessarily affect the structure of the residue and the sludge, it may be predicted that they will yield results which need not necessarily correlate with the true sludge content of the fuel.

Thus the " Bottom, Sediment and Water Test " (A.S.T.M. Method 96–35, Bureau of Mines Method 300.32) employs benzene as a diluent. This undoubtedly dissolves parts of the sludge which may cause difficulties under special conditions.

The methods proposed for removing sludge from cracked residues generally entail a filtration of the material—either as such, or after treatment with a coagulant (for instance an acid)—or else aim at a conversion of the sludge into an innocuous form by stabilization or peptization.

The investigation now to be described may conveniently be divided into three parts. The first gives details of a qualitative microscopical examination, and contains a discussion of the hypotheses used to gain an insight into the structure of cracked residues; in the second part a method is described for the quantitative determination of the actual sludge present in a cracked residue or fuel, and in the third part the heating stability of the cracked residue is discussed.

Qualitative Microscopical Examination.

If a layer, with a thickness of, say, 0·03 mm., of a cracked residue is examined under a microscope, employing ordinary (direct) illumination and slight enlargement, the field will generally be seen to contain varying numbers of dark, angular fragments. Microphotographs in Figs. 1 and 4 show the appearance of two fuels, *A* and *B* (cracked residues from paraffin-base stock), under these conditions. Fig. 3 is a similar photograph taken with a five times greater enlargement.

A close observer will distinguish a quantity of scarcely visible, finely divided particles between these fragments. This matter, however, becomes clearly apparent when dark-field illumination is employed.* Frequently the field of vision is then seen to be almost filled with inhomogeneities. Figs. 2 and 5 correspond to Figs. 1 and 4 (cracked residues *A* and *B*), respectively, and illustrate the complete alteration in appearance.

The particles thus revealed are of varying size. Observations with strong magnifications (*e.g.* 900 ×) frequently show the presence of small particles in a state of slow Brownian motion. The larger particles often appear to be floccules composed of smaller components. In the case of a cracked residue from a paraffin-base stock, the use of crossed Nicols brings to light a quantity of doubly-refracting material (paraffin and ceresin), as shown in Fig. 6.

Cracked residues from asphalt-base stocks show all the above characteristics, except for the presence of doubly-refracting matter (see Figs. 7, 8 and 9 of two residues *C* and *D*). Generally, the microscopic images differ widely. Sometimes the whole field is seen to be covered with particles, as

* In their microscopical work employing dark-field illumination, the authors made use of a Zeiss " preparation " condenser (N.A. 0, 3) for low powers, and a Zeiss cardioid condenser (N.A. 1, 0) for strong enlargements.

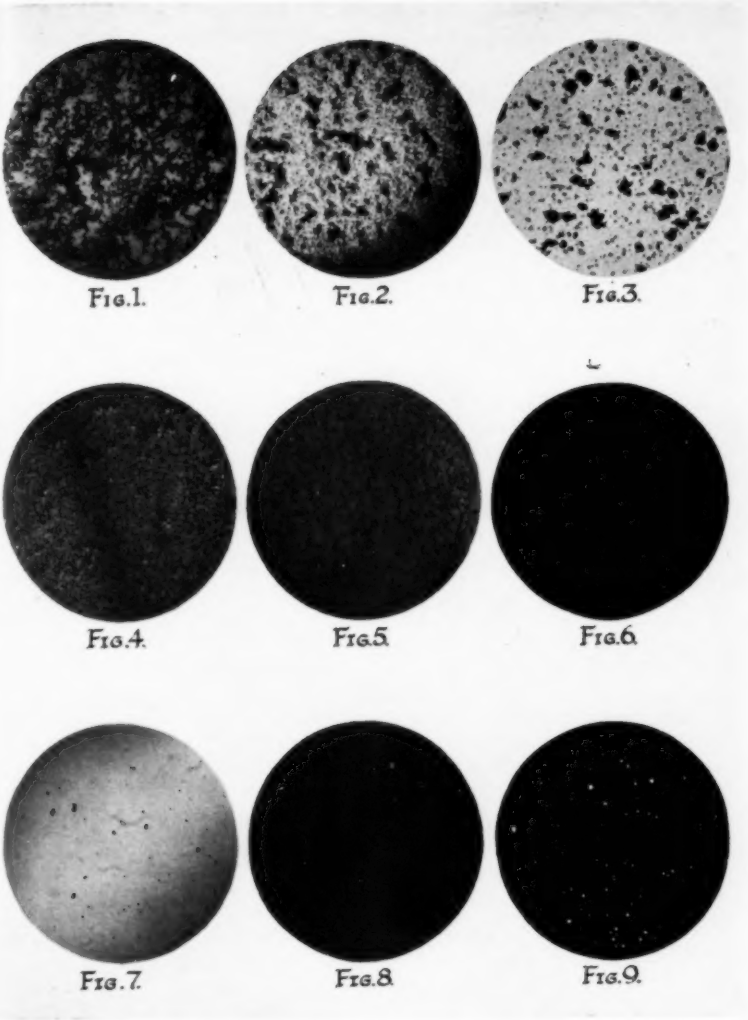

Fig. 1.—Cracked residue A, large in object glass about 0·03 mm. thick, bright field illumination. (41 ×).
Fig. 2.—Cracked residue A, dark field illumination. (41 ×).
Fig. 3.—Cracked residue A, bright field illumination. (205 ×).
Fig. 4.—Cracked residue B, bright field illumination. (41 ×).
Fig. 5.—Cracked residue B, dark field illumination. (41 ×).
Fig. 6.—Cracked residue B, crossed nicols. (41 ×).
Fig. 7.—Cracked residue C, bright field illumination. (41 ×).
Fig. 8.—Cracked residue C, dark field illumination. (41 ×).
Fig. 9.—Cracked residue D, dark field illumination. (41 ×).

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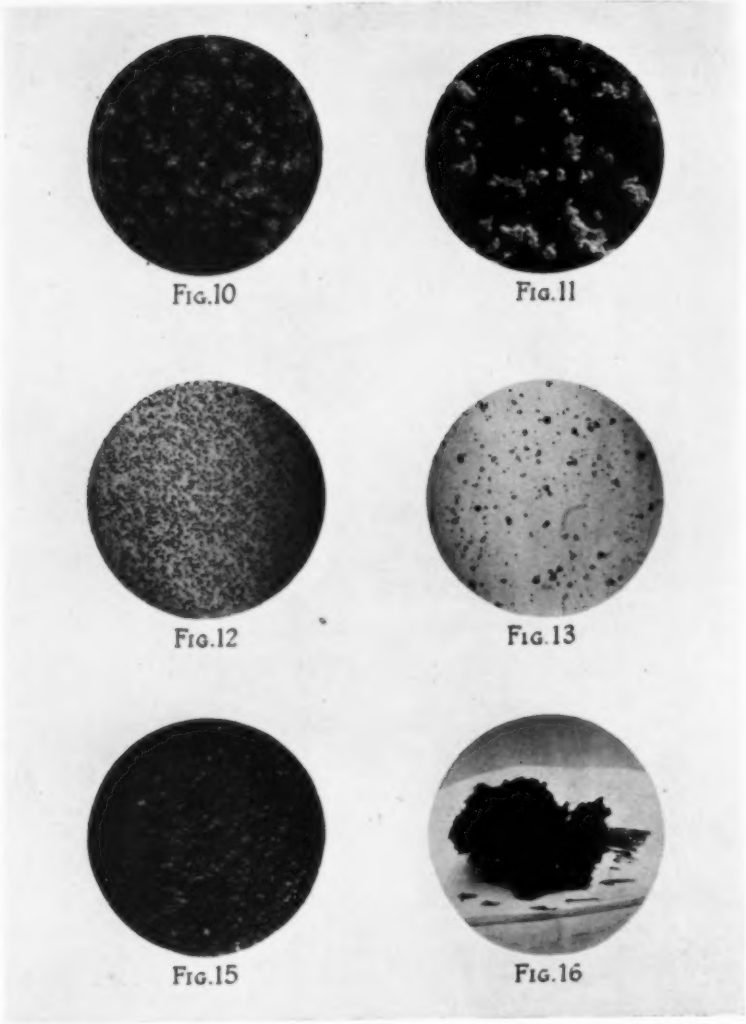

FIG. 10.—Cracked residue D, after adding aromatic-free 60/80 gasoline. (41 ×).
FIG. 11.—Straight-run residue E, after adding aromatic-free 60/80 gasoline. (41 ×).
FIG. 12.—Cracked residue A, freed from the carbonaceous particles after heating for 10 days at 100° C. (bright field illumination).
FIG. 13.—Residue C, treated as indicated for Fig. 12.
FIG. 15.—Residue C, diluted with gas oil (1 : 1), bright field illumination.
FIG. 16.—Sludge, centrifuged from residue C, diluted with gas oil (1 : 1).

in Figs. 2 and 5, and sometimes scarcely any material is to be seen at all, not even with dark-field illumination. The writers have come to the conclusion that this depends on the nature of the residues, and especially on the depth of the cracking. Residues cracked to a high specific gravity, for instance, contain much visible material, and those cracked to a low specific gravity very little.

In the case of straight-run residues, nothing is as a rule seen in direct and dark-field illumination, but wax crystals (and an occasional crystal of an inorganic material, *e.g.* salt) may become apparent between crossed Nicols.

The Influence of Solvents.

(*a*) *Benzene.* If a little c.p. benzene is dropped on the residue upon the object slip—in a proportion of, say, 1 : 1—and the two materials are mixed with a rod, it will be seen through the microscope that a considerable portion of the particles visible in dark-field illumination dissolve, whilst the dark, angular fragments remain unaffected. These fragments are the "coke" met with in practice, and it is principally the proportion of this material which is diminished by modern cracking methods. (The change may sometimes be from 30 per cent. to less than 1 per cent.) The same fragments, together with entrained medium, are responsible for the sludge found in the B.S. & W. test.

If a large dilution (*e.g.* 1 : 9) in benzene is examined, it may, however, be found that a part of the dissolved matter again separates. It is interesting to watch this process with dark-field illumination. In the field of vision, at first "empty," minute particles in violent Brownian motion are seen to appear. The particles gradually increase in size, the Brownian movement diminishes, finally ceases, and the field is again filled with motionless particles.

In the experiments subsequently described here, it has been customary to employ residues from which the carbonaceous particles (which are of relatively little interest) have been separated by centrifuging from a 1 : 1 solution in benzene.

(*b*) *Aromatic-free* 60/80 *Spirit.* If a cracked residue is diluted under the microscope with aromatic-free 60/80 spirit, a different process is observed. The particles visible in dark-field illumination are seen to conglomerate, and at the same time new particles appear, which may almost fill the whole field of vision (see Fig. 10). Upon evaporation of the solvent, a considerable part of the separated matter again dissolves.

A very similar phenomenon (when 60/80 spirit in an excess is used as a diluent) is also seen in the case of a straight-run residue (see Fig. 11).

The material separated by 60/80 spirit from a residual material is referred to in petroleum terminology by the term "flocculated asphaltenes," and so for the time being the flocculated material in the cracked residues may be designated as "flocculated asphaltenes." Very little is known about these substances, except that they are presumably in the main hydrocarbons of an aromatic character and unsaturated.

The Influence of Heating.

If a cracked residue is heated on a microscope provided with a heatable stage,* it will be observed in dark-field illumination that a considerable percentage of the particles (flocculated asphaltenes) dissolves in the medium. (The carbonaceous matter, as may be expected, does not dissolve, even up to temperatures at which decomposition sets in.) The temperature at which the flocculated asphaltenes dissolve is to a great extent dependent on the nature of the cracked residue, as may be illustrated by taking the case of the four products (*A* and *B* from paraffin-base stock, *C* and *D* from asphalt-base stock) already referred to.

Residue A.—The larger particles vanished at 130–140° C. The process of solution continued to 200° C., when no further solution took place; the remaining particles were evenly distributed.

Residue B.—Solution commenced at 120° C., and increased rapidly at 150° C. At 190° C. nearly all particles had dissolved.

Residue C.—Solution took place rapidly in the range 80–90° C. A few larger particles remained undissolved.

Residue D.—Solution range: 80–90° C. A few particles remained.

Some tentative experiments were carried out in order to obtain an impression of the influence exerted by cracking conditions on the solution temperature. The asphaltic-base material of residue *C* was cracked in an autoclave, provided with a stirrer, for 15 min. at various temperatures, and the cracked residues were microscopically examined. The results are given below, and indicate—as might be expected—that an increase in the severity of the cracking conditions renders the particles more difficult to dissolve.

Temperature of Cracking, ° C.	Temperature of Complete Solution of Particles.
428	abt. 200
405	„ 140
380	„ 80

On cooling the residues which have been rapidly heated to the solution temperature, particles again appear after a certain period.

If the residues are heated to a moderate temperature (*e.g.* 100° C.) for a considerable length of time, such as from 7 to 10 days, another phenomenon occurs, which may be described as a commencement of secondary and *irreversible flocculations*. The particles coalesce into flakes and appear to be more firmly combined, with the result that they gradually assume the appearance of the carbonaceous particles referred to above. In this condition they tend to lose their ability to be re-dispersed by the medium or by benzene. Thus residue *A* (which originally contained 2·1 per cent. of matter that could be centrifuged out from a 1 : 1 benzene solution) after 10 days' heating at 100° C. gave a corresponding figure of 4·0 per cent. The appearance of residues *A* and *C* after this treatment is shown in Figs. 12

* See, for instance, "A Simple Arrangement to Demonstrate Liquid Crystals" in *Liquid Crystals and Anisotropic Melts* (a general discussion held by the Faraday Society, April 1933), p. 915.

and 13. Naturally this process only takes place *when the solution temperature is above that at which heating is effected.* The phenomena will be discussed at greater length later.

With increasing age there is also a tendency for a secondary flocculation to occur in a cracked residue. This process, however, does not proceed so far as that produced by prolonged mild heating, and the particles remain dispersable in benzene. In many cases ageing is also accompanied by a continuous increase in the quantity of flocculated asphaltenes, as a result of the formation of new particles by primary flocculation.

Theoretical Considerations.

In order to explain the phenomena observed, a few assumptions which have served as a working hypothesis may be detailed here.

Cracked residues, in the same way as asphalts, may be regarded as colloidal systems, in which the dispersed phase consists of the "asphaltenes," *i.e.* polymerized hydrocarbons which in the main are very probably of an

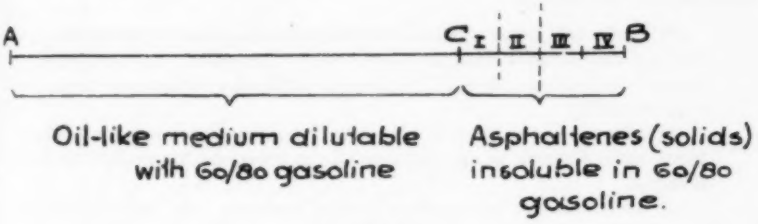

Fig. 14.

DIAGRAM OF THE COMPOSITION OF STRAIGHT-RUN AND CRACKED RESIDUES.

aromatic character considering their low hydrogen content. (The C : H ratio may amount to about 10 in the case of asphaltene fractions from straight-run products and to 15 in the case of asphaltenes from cracked residues.)[1,2] These "asphaltenes" are an essential component of petroleum residues (asphalts, straight-run and cracked residues), and are the cause of the "colloidal" properties of these residues, such as plasticity, elasticity, gelatination, etc.

If the asphaltenes are extracted with solvents having continually increasing solvent capacity, the C : H ratio of the first extract is invariably lower than that of the next. The asphaltene fraction, therefore, consists of a mixture of materials. The part with the highest C : H ratio is the most strongly condensed and the most difficult to dissolve. In the residue it can only dissolve in components to which it is closely related, so in that part of the asphaltene fraction of which the C : H ratio is slightly lower. This fraction, in its turn, will only be soluble in the fraction with again a lower C : H ratio, and so on.

If no sludge is present the system can be represented by the diagram in Fig. 14.

The line *AB* shows the composition of the residue. The part *AC* is the oil-like medium containing what is known as the resins. The part *BC* is

the asphaltenes dispersed in the medium. The part marked IV is dispersable in III, the latter in II, and so on. It may happen that one of the parts (in the diagram the part marked II) is missing (for instance, owing to the conditions of cracking or to the composition of the base material), so that III and IV cannot be kept in solution, and consequently flocculate. Moreover, a diluent added to the system may only be miscible as far as II (inclusive). This also promotes separation and III and IV precipitate, entraining a little dispersion medium. In the example discussed, III and IV are therefore the " sludge " (visible under the microscope).

Flocculation may be reversible, *i.e.* upon heating, the sludge may dissolve, if II is present, in weak concentrations. If the concentration of II becomes too weak irreversible flocculation occurs.

What is now the difference between a cracked and an uncracked residue —in other words, what has occurred in the cracking process to produce the phenomena described (*i.e.* the ability to liberate sludge under various conditions)?

Presumably, there are several factors in cracking which contribute to the tendency to form sludge.

(*a*) There will be progressive dehydrogenation and condensation of existing asphaltenes, making them more condensed. This chemical change and perhaps physical increase in molecular dimensions decrease their solubility.

(*b*) There is an increase in the quantity of asphaltenes, new asphaltenes being formed, at the expense of the less dehydrogenated hydrocarbons.

(*c*) An alteration takes place in the medium. On the one hand, less dehydrogenated products, which act as stabilizers, are converted into asphaltenes, and, on the other hand, aromatic molecules with side-chains undergo fissure, producing a more aliphatic medium of higher flocculating tendency.

Dilution of Cracked Residues with Gas Oils.

The dilution of cracked residues with gas oils is very frequently resorted to in refinery practice, and it will be apparent from the foregoing that the results will be dependent on the nature of the diluent employed, *i.e.* gas oils may have a flocculating (or precipitating) tendency or may act as stabilizers. (They may also conceivably be neutral in action.)

Figs. 15 and 16 illustrate the typical precipitating action of a certain gas oil on residue *C*. The diluted residue in this case showed no true solution temperature (particles being present up to 200° C.), and here again prolonged heating to 100° C. gave rise to a " cementation " of the particles and irreversible flocculation.

Quantitative Determination of Sludge.

From now on we shall refer to the flocculated asphaltenes, together with the carbonaceous material, as " sludge."

As stated in the introduction, almost all methods proposed for determining sludge make use of a diluent, and it will now be obvious that a single

experiment carried out in such a fashion cannot give us information as to the true sludge content of the sample.

Attempts which the authors made to determine the sludge by direct filtration or centrifuging proved failures in most cases, owing to the fine state of dispersion of the particles and the viscosity of the medium. A method has, however, been developed which permits of determining this sludge by an indirect procedure.

If a certain quantity (by weight) of residue is diluted with increasing volumes of a precipitant liquid (*e.g.* 60/80 gasoline), increasing quantities of precipitate are obtained. If the percentages of precipitate are plotted as a function of the volumes of precipitant hydrocarbon, we obtain what are known as the precipitation curves.

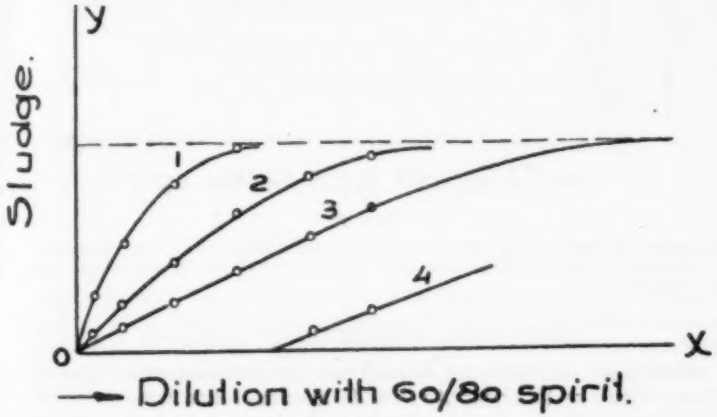

FIG. 17.

RELATION BETWEEN THE PERCENTAGE OF ASPHALTENES IN THE CRACKED AND STRAIGHT-RUN RESIDUES AND THE DILUTION WITH 60/80 GASOLINE. NO SLUDGE PRESENT.

When precipitation figures are determined in this manner on a number of residues, curves are obtained of the type shown in Figs. 17 and 18. All the curves appear to approach a maximum asphaltene value asymptotically, but it will be apparent that the initial parts of the curves differ considerably. In Fig. 17 the three curves 1, 2 and 3 are all drawn to commence at the origin, and hence they represent residues which, at zero dilutions, contain no sludge, but which commence to precipitate "asphaltenes" immediately after dilution is started. They are further represented as all three tending towards the same maximum "asphaltene" value, but differing in initial slope. In such cases it may be assumed that though the total amount of asphaltenes is the same, the degree of stabilization towards 60/80 spirit differs, 3 being better stabilized than 2, and 2 better than 1.

Curve 4 represents a case where a certain amount of initial dilution is required to precipitate the first "asphaltenes." This case is exemplified in practically all straight-run residues.

In Fig. 18 the two curves illustrate what is met with in the case of many cracked residues: the curves, extrapolated to zero dilution, show a positive sludge value, and it is obvious that the process of extrapolation gives us a valuable method of conveniently determining this sludge figure.

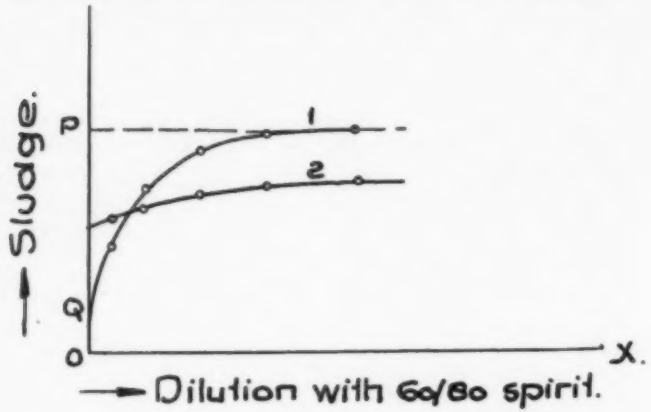

FIG. 18.

RELATION BETWEEN THE PERCENTAGE OF ASPHALTENES IN THE CRACKED AND STRAIGHT-RUN RESIDUES AND THE DILUTION WITH 60/80 GASOLINE. SLUDGE PRESENT.

EXPERIMENTAL DETERMINATION OF SLUDGE.

About 5 gm. of residue are weighed into graduated centrifuge glasses and diluted with a certain quantity of 60/80 gasoline. For instance, 4·396 gm. are diluted with 4·4 ml. of gasoline at a dilution ratio of 1 : 1, with 8·8 ml. of gasoline at a dilution ratio of 1 : 2, etc. The mixture is well shaken and centrifuged at a high rate of r.p.m. (2500–3000 r.p.m.) until all the precipitate is deposited at the bottom of the centrifuge glass. The top liquid is decanted off, fresh spirit is added, the contents of the tube are mixed and again centrifuged, washing and centrifuging being continued until the washings are a pale yellow. The resulting precipitate is finally dissolved in benzene, evaporated, dried at 110° C. and weighed.

An error is made in such determinations by the fact that the mediums present in the separated asphaltenes will give rise to further precipitation with the wash-liquid, but this error can be diminished by using a correction formula.

This formula is derived as follows.

If V is the volume of the precipitate, consisting of precipitated asphaltenes and entrained medium, and g is the true quantity of precipitated asphaltenes (specific gravity about 1), then $(V - g)$ ml. is the volume of the entrained medium, consisting of material diluted with gasoline and partly liberated of asphaltenes. If the quantity of residue (or fuel) weighed is E (in grammes or in millilitres, for the specific gravity is about 1) and x the coefficient of dilution ($x = 1$ if dilution ratio is 1 : 1, $x = 2$ if the dilution ratio is 1 : 2,

and so on) then $(E + xE)$ ml. is the total volume of the mixture and $(E + xE - g)$ ml. is the volume of the mixture from which the asphaltenes have been partly eliminated. If T is the percentage of asphaltenes at a high rate of dilution, then $\left(\frac{E \,.\, T}{100} - g\right)$ is that quantity of asphaltenes that was not precipitated in the dilution of $1 : x$. This quantity is therefore present in the volume $(E + xE - g)$ ml. of the medium. In the medium, which is entrained by the precipitate, there is therefore present $\frac{(V - g) \,.\, \left(\frac{E \,.\, T}{100} - g\right)}{(E + xE - g)}$ gm. of asphaltenes, which is precipitated during washing and which is weighed besides the true content g.

If, therefore, A gm. of asphaltenes is weighed

$$A = g + \frac{(V - g)\left(\frac{E \,.\, T}{100} - g\right)}{(E + xE - g)}$$

and therefore the true weight is

$$g = \frac{AE(1 + x) - \frac{E \,.\, T \,.\, V}{100}}{E(1 + x) + A - V - \frac{ET}{100}}$$

Therefore, after the precipitate has been centrifuged off, the volume is read off from the centrifuge glass, the values found are filled in the correction formula, and the true percentage of asphaltenes precipitated is calculated.

The percentages calculated are then plotted as a function of the dilution—for instance, the dilution on the x axis and the percentages on the y axis. A smooth curve is then drawn through the points found, and this is extrapolated to the y axis.

It will soon be seen that this extrapolation leads to difficulties if the beginning of the curve rises steeply. The use of less strong precipitants may then be resorted to—for instance, mixtures of gasoline and benzene. The lines then become flatter, and extrapolation is facilitated. At a certain concentration of benzene in the gasoline the precipitation line is practically horizontal and, naturally, at this mixture the quantity of sludge can be *determined directly*, as this liquid is neutral with respect to the sludge. This liquid may also be used as " neutral " washing liquid when washing out the precipitates.

The writers also tried to express the curves in empirical formulæ so as to carry out the extrapolation mathematically. If the curve was not too steep, the following formula could be applied satisfactorily, with sufficient accuracy.

$$y = a(1 - 10^{-kx}) + b \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$y b$ = the percentage of precipitate at a dilution of x.
$a +$ = the percentage of precipitate at very high dilution ($x = 100$).
b = sludge content ($x = 0$).
k = a constant.

In certain cases the following formula could be applied:

$$\frac{1}{a-y} = kx + \frac{1}{a-b} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

y = the percentage of precipitate at a dilution of x.
a = the percentage of precipitate at very high dilution.
b = sludge content.
k = a constant.

Examples.

1. A flash fuel P was diluted in the manner described above with various volumes of 60/80 gasoline, and the percentages of asphaltenes were determined. In one test the fuel was washed with plain gasoline without using the correction formula, and in the second test the fuel was washed with neutral washing liquid consisting of 1 vol. of benzene and $2\frac{1}{4}$ vols. of gasoline. The results are given in Table I.

TABLE I.

Washed with Gasoline.		Washed with the Neutral Washing Liquid.	
Dilution.	Percentage of Asphaltenes.	Dilution.	Percentage of Asphaltenes.
		1 : 0 *	1·6
1 : 1	4·2	1 : 1	3·5
1 : 2	5·15	1 : 2	4·75
1 : 3	5·9	1 : 3	5·6
1 : 10	7·0	1 : 7	7·0

* The sludge was here directly determined by diluting 1 volume of flash fuel with 2 volumes of neutral washing liquid.

The results are plotted on Fig. 19. The results in the second column are clearly too high (dotted line). Those in the fourth column are correct (full line). The extrapolated sludge content corresponds to that determined directly.

If the results of column 2 are corrected with the aid of the formula, they coincide with the full-drawn curve. At a dilution ratio of 1 : 1, if the symbols of the correction formula were used:

$E = 3{\cdot}915$ gm. $\qquad A = 0{\cdot}165$ gm.
$T = 7{\cdot}0$ per cent. $\qquad V = 1{\cdot}5$ ml.

At a dilution ratio of 1 : 3 :

$E = 5{\cdot}174$ gm. $\qquad A = 0{\cdot}305$ gm.
$T = 7{\cdot}0$ per cent. $\qquad V = 3{\cdot}0$ ml.

If these values are substituted in the correction formula, g, at a dilution ratio of 1 : 1, = 0·142 gm. = 3·6 per cent., and, at a dilution ratio of 1 : 3, = 0·296 gm. = 5·7 per cent. It was found that the curve complied with the empirical formula (1) in which

$k = 0{\cdot}21$
$a = 5{\cdot}4$ per cent.
$b = 1{\cdot}6$,, ,,

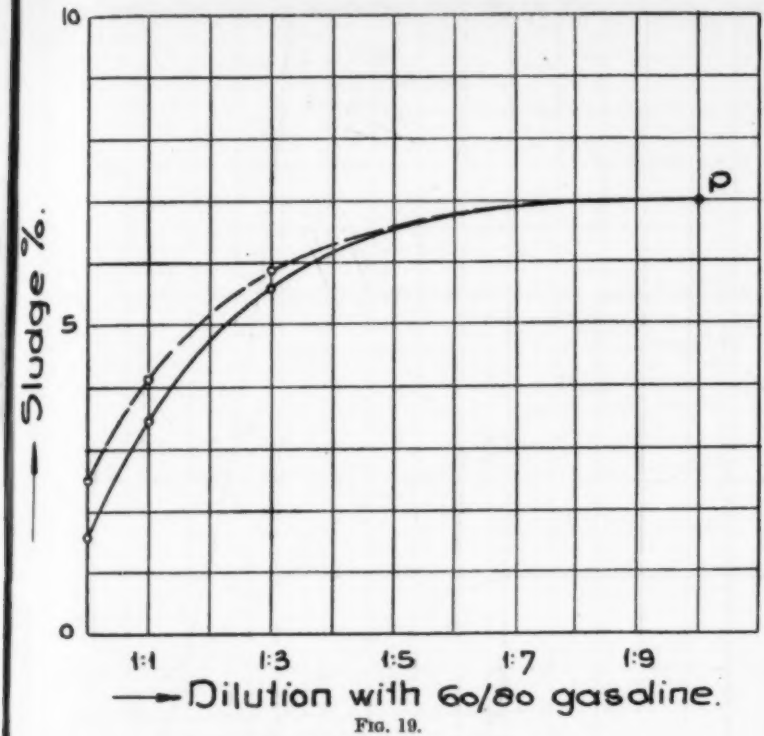

FIG. 19.

PRECIPITATION CURVES OF FLASH FUEL P.

- - - - curve obtained after washing the precipitates with plain gasoline, without applying the correction formula.

——— curve obtained after washing the precipitates with neutral washing liquid, or applying the correction formula.

2. Cracked residue *A* (Figs. 1 and 2) was treated with various volumes of aromatic-free gasoline, and the percentages of asphaltenes were determined, applying the correction formula. The results are given in Table II and plotted in Fig. 20 (curve *A*).

TABLE II.

Dilution.	Asphaltene Content, %.
1 : ½	6·9
1 : 1	7·5
1 : 2	8·2
1 : 3	8·5
1 : 20	9·0

Upon extrapolation the sludge content was found to be 6·2 per cent.

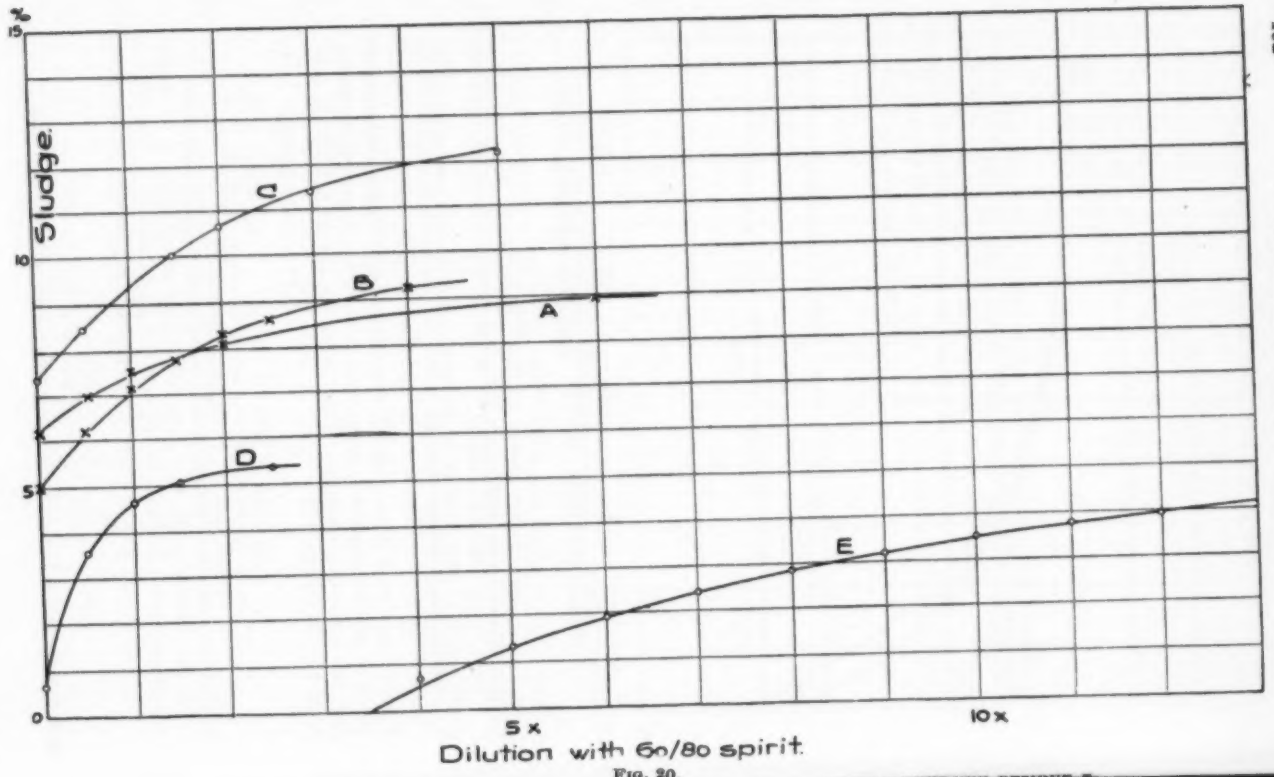

Fig. 20.

This
which

This curve was also in accordance with the empirical formula (1) in which

$k = 0{\cdot}25$
$a = 2{\cdot}8$ per cent.
$b = 6{\cdot}2$ „ „

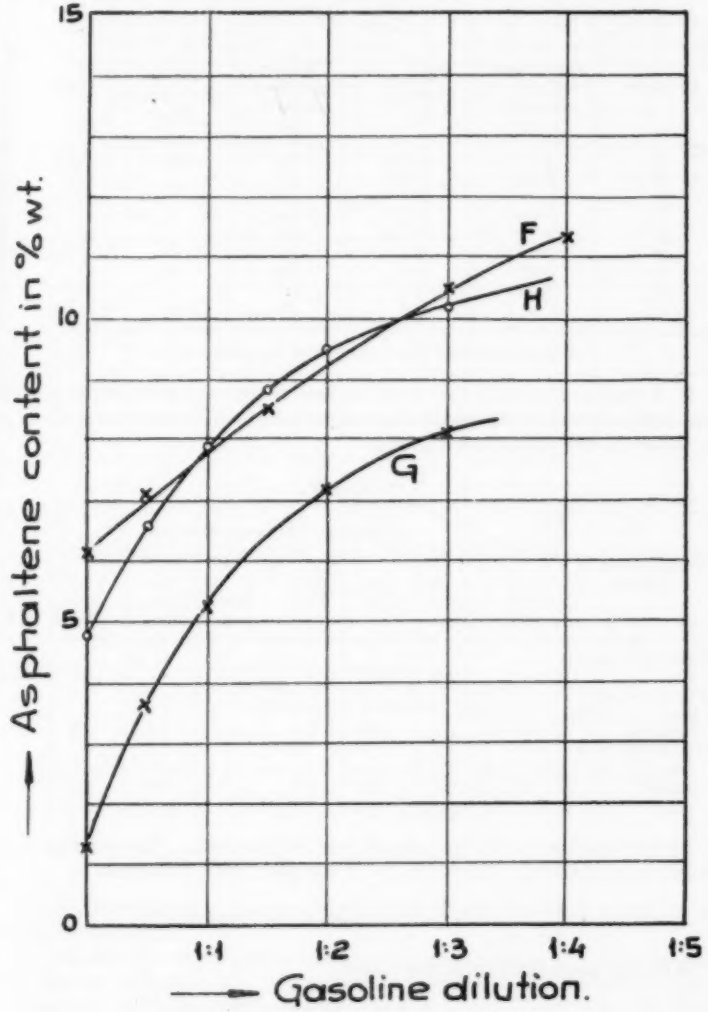

FIG. 21.

PRECIPITATION CURVES OF THE CRACKED RESIDUES F, G AND H.

Dilution with 60/80 spirit.
FIG. 20.

In this residue the percentage of insoluble matter was also determined if the residue was diluted in a ratio of 1 : 1 with benzene. The result was found to be 2·1 per cent.

3. In the same manner the sludge content of residues *B*, *C*, *D*, *E*, *F*, *G* and *H* were determined, the results, with these products with the two previous, being given in Table III and plotted in Figs. 20 and 21.

TABLE III.

Product.	Percentage Insoluble in Benzene 1 : 1.	Sludge Content, %.	Total Asphaltene Content, %.	Micro-photographs Figs.	Curve.
A	2·1	6·2	9·0	1 and 2	Fig. 20
B	0·05	5·0	9·6	4 „ 5	„
C	0·16	7·4	12·7	7 „ 8	„
D	0·08	0·7	5·4	9 „ 10	„
E *	0	0	4·4	—	„
F	0·15	6·1	16·1	—	Fig. 21
G	0·08	1·3	9·1	—	„
H	0·40	4·8	11·0	—	„
P	—	1·5	7·0	—	Fig. 19

* *E* was a straight-run residue and base material of *C*.

4. A residue *Q* was treated with various volumes of plain 60/80 gasoline and with mixtures of 60/80 gasoline and benzene. The results are collected in Table IV and plotted on Fig. 21*a*.

TABLE IV.

Composition of Mixture.	Percentage of Precipitate with :							
	1 : 1 Dilution.	1 : 2 Dilution.	1 : 3 Dilution.	1 : 4 Dilution.	1 : 4½ Dilution.	1 : 5 Dilution.	1 : 6 Dilution.	1 : 100 Dilution.
Plain 60/80 gasoline	9·4	10·8	11·3	—	11·7	—	12·1	12·5
90% 60/80 gasoline, 30% benzene	—	5·9	6·7	6·9	—	7·2	7·6	9·1
80% 60/80 gasoline, 35% benzene	3·9	4·7	5·5	6·0	—	—	6·4	7·6

In this residue the sludge content was 3·0 per cent. Curve 3 was extrapolated graphically. Curves 1 and 2 complied with a formula :

$$\frac{1}{a-y} = kx + \frac{1}{a-b} \text{ (empirical formula (2))}$$

With the plain 60/80 gasoline added :

$$b = +\ 3{\cdot}0 \text{ per cent.}$$
$$a = +\ 12{\cdot}5 \text{ „ „}$$
$$k = \quad 0{\cdot}218$$

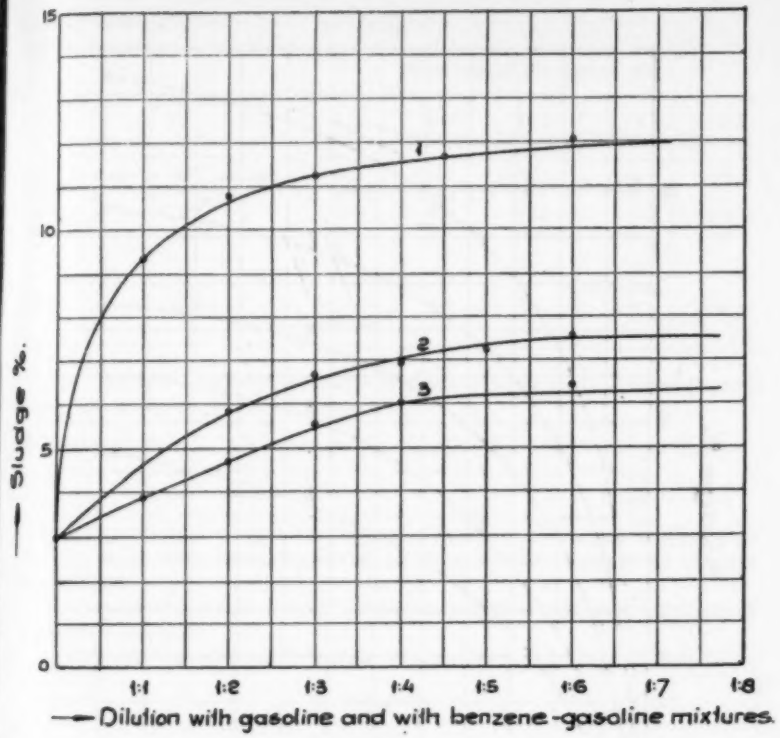

FIG. 21a.

PRECIPITATION CURVES OF CRACKED RESIDUE Q WITH 60/80 GASOLINE AND WITH MIXTURES OF 60/80 GASOLINE AND CHEMICALLY PURE BENZENE.

1. 100% 60/80 gasoline.
2. 30% benzene + 70% 60/80 gasoline.
3. 35% benzene + 65% 60/80 gasoline.

With the mixture of 30 per cent. benzene and 70 per cent. gasoline :

$$b = +3{\cdot}0 \text{ per cent.}$$
$$a = 9{\cdot}1 \quad ,, \quad ,,$$
$$k = 0{\cdot}072$$

Hence, with three different precipitants, about the same point on the y axis is reached.

5. Residue R was treated in the same way as residue Q. This example was chosen, however, on account of its being a cracked residue with a "negative" sludge content—that is to say, a certain quantity of precipitant was required before the first precipitate was formed.

The results are given in Table V and plotted on Fig. 22.

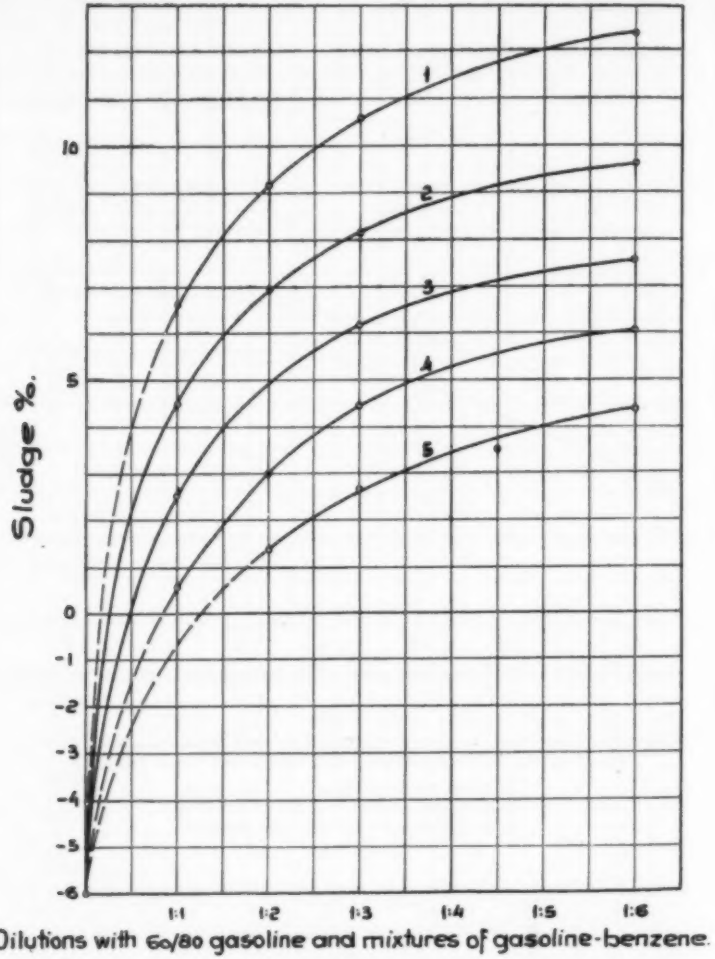

FIG. 22.

PRECIPITATION CURVES OF CRACKED RESIDUE R WITH 60/80 GASOLINE AND WITH MIXTURES OF 60/80 GASOLINE AND CHEMICALLY PURE BENZENE.

1. 10% benzene + 90% gasoline 60/80.
2. 20% benzene + 80% gasoline 60/80.
3. 30% benzene + 70% gasoline 60/80.
4. 40% benzene + 60% gasoline 60/80.
5. 50% benzene + 50% gasoline 60/80.

TABLE V.

Composition of Mixture.	Percentage of Precipitate with:				
	1 : 1 Dilution.	1 : 2 Dilution.	1 : 3 Dilution.	1 : 6 Dilution.	1 : 100 Dilution.
10% benzene + 90% gasoline	6·7	9·2	10·6	12·4	14·0
20% „ + 80% „	4·5	7·0	8·2	9·6	11·1
30% „ + 70% „	2·6	5·4	6·2	7·6	9·4
40% „ + 60% „	0·6	3·0	4·5	6·1	7·4
				1 : 4½ Dilution.	
50% „ + 50% „	No precipitate	1·4	2·7	4·4	6·5

The " negative " sludge content was about — 6 per cent. Curves 2 and 3 complied with the empirical formula (2).

In curve 2 : b = — 6·0 per cent. a = 11·1 „ „ k = 0·094

In curve 3 : b = — 6·0 per cent. a = 9·4 „ „ k = 0·082

6. The method also applies in the case of mixtures of cracked residues with gas oil, as in most cases the sludge in these mixtures cannot be directly centrifuged.

Thus cracked residues *B* and *C* were diluted with various proportions of (different) gas oils.

The results are collected in Tables VI and VII and in Figs. 23 and 24.

TABLE VI.

Product.	Insoluble in Benzene 1 : 1, %.	Sludge Content, %.	Total Asphaltene Content, %.	Curve.
Residue *B*	0·05	5·0	9·6	1 in Fig. 23
90% res. *B* + 10% gas oil	0·07	4·5	8·3	2 „ „
70% „ + 30% „	0·11	3·9	6·0	3 „ „
50% „ + 50% „	0·50	3·3	4·5	4 „ „
30% „ + 70% „	0·27	2·5	2·7	5 „ „
10% „ + 90% „	0·11	0·8	1·0	6 „ „

TABLE VII.

Product.	Insoluble in Benzene 1 : 1, %.	Sludge Content, %.	Total Asphaltene Content, %.	Curve.
Residue *C*	0·16	7·4	12·7	1 in Fig. 24
90% res. *C* + 10% gas oil	0·16	6·1	11·3	2 „ „
70% „ + 30% „	0·13	4·6	8·9	3 „ „
50% „ + 50% „	0·15	3·2	6·1	4 „ „
30% „ + 70% „	0·38	2·1	3·7	5 „ „
10% „ + 90% „	0·26	0·8	1·2	6 „ „

In Figs. 25 and 26 the sludge content and the total asphaltene content have been plotted as a function of the dilution in gas oil.

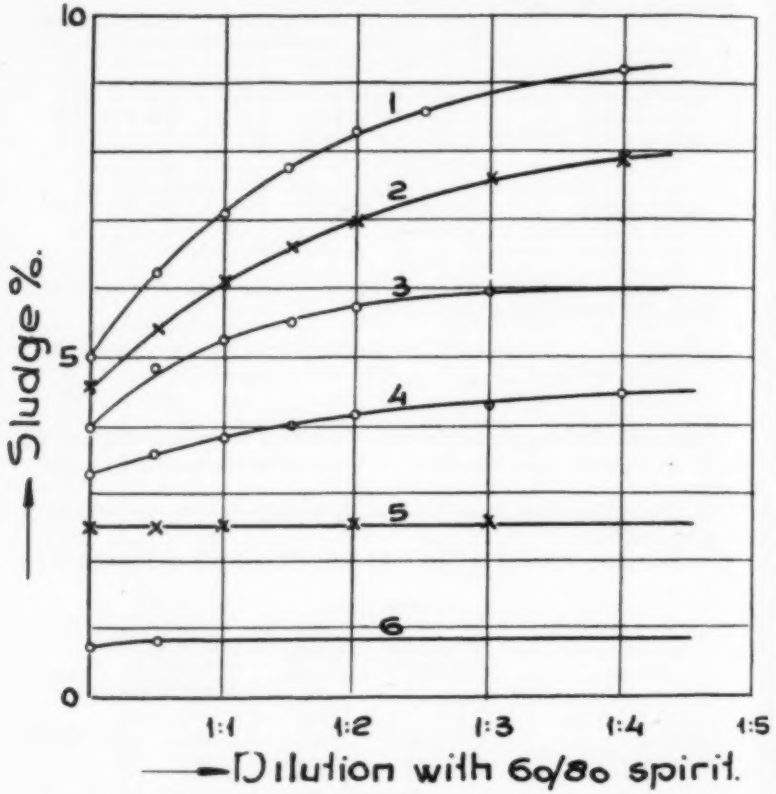

FIG. 23.

PRECIPITATION CURVES OF THE CRACKED RESIDUE B AND MIXTURES OF THIS WITH DIFFERENT PERCENTAGES OF GAS OIL.

1. Undiluted residue.
2. 90% residue + 10% gas oil.
3. 70% residue + 30% gas oil.
4. 50% residue + 50% gas oil.
5. 30% residue + 70% gas oil.
6. 10% residue + 90% gas oil.

Taking Fig. 26 first, it will be noticed that the points for the sludge lie almost on a straight line. In other words, the gas oil here merely diluted the fuel in a neutral fashion, no additional sludge being flocculated and no sludge being peptized. The total asphaltene content also lies, as it theoretically should, on a straight line.

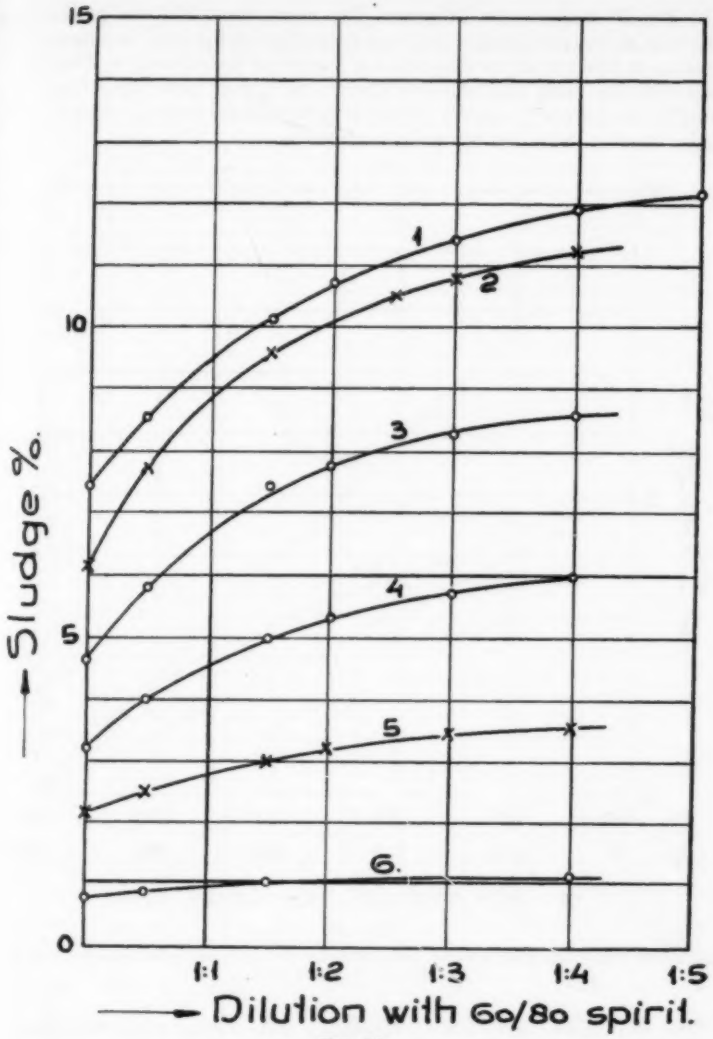

FIG. 24.

PRECIPITATION CURVES OF THE CRACKED RESIDUE C AND MIXTURES OF THIS WITH DIFFERENT PERCENTAGES OF GAS OIL.

1. Undiluted residue.
2. 90% residue + 10% gas oil.
3. 70% residue + 30% gas oil.
4. 50% residue + 50% gas oil.
5. 30% residue + 70% gas oil.
6. 10% residue + 90% gas oil.

In Fig. 25 matters are different. The curve for initial sludge lies considerably above the straight line connecting its end-points, and hence the addition of this gas oil to this fuel has a decided flocculating action. The points for the total asphaltene content also depart somewhat from the straight line (probably mainly owing to experimental errors), but not sufficiently so as to upset the value of the method.

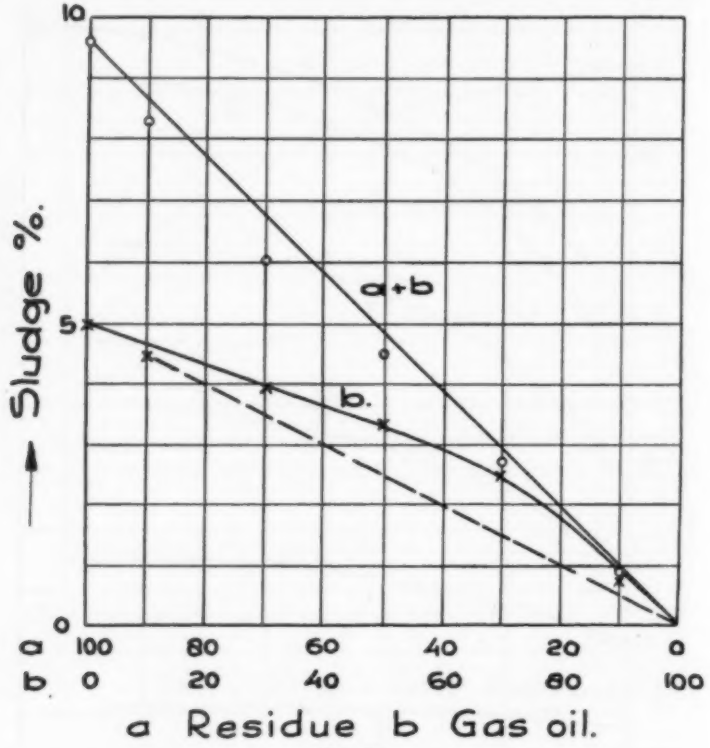

FIG. 25.

RELATION BETWEEN THE SLUDGE AND ASPHALTENE CONTENTS OF VARIOUS GAS OIL DILUTIONS OF RESIDUE B.

THE STABILITY OF CRACKED RESIDUES AND FUELS UPON HEATING.

The stability of residues and fuels upon heating is very important, as in practice, before the fuels are atomized in the burners they are heated in the preheaters. A coat of carbonaceous matter is very frequently deposited on the preheater tubes, and this may sometimes assume serious proportions if unstable cracking fuels are used.[3]

After considering these points, the investigator, of course, immediately wonders whether there is any direct relation between the sludge content

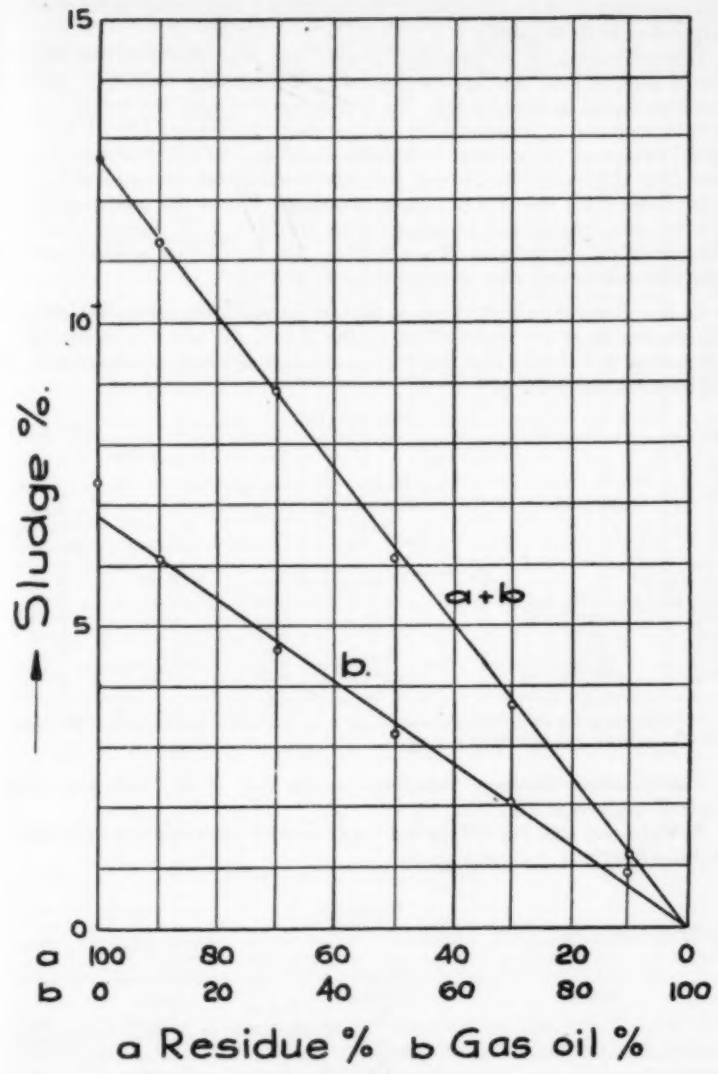

FIG. 26.

RELATION BETWEEN THE SLUDGE AND ASPHALTENE CONTENTS OF VARIOUS GAS OIL DILUTIONS OF RESIDUE C.

and the heater-coating difficulties encountered with residues and fuels. This question must be answered in the negative: there is no direct relationship between these points.

When studying the subject more closely, one must therefore compare the sludge figures with the figures expressing the heating stability. Now, it has been found in practice that the increase of the part of a residue or fuel that is insoluble in benzene after heating it for 10 days at 100° C. is a very useful means of expressing the heating stability. If this increase is large, therefore, the residue or the fuel has poor heating stability, and vice versa.

In Table VIII the sludge figures of residue *B* and the mixtures of this residue with gas oil are compared with the B.S. & W. figures (A.S.T.M. Method 96–35, Bureau of Mines Method 300.32) of this residue and the mixtures before and after heating them to 100° C.

(N.B.—It must be borne in mind that no quantitative agreement between the figures must be expected, as in the B.S. & W. test the *volume* of the precipitate is recorded and this volume consists not only of sludge but also of the entrained medium.)

TABLE VIII.

Product.	Sludge Content, %.	B.S. & W.*		
		Before Heating.	After 6 Days' Heating.	After 10 Days' Heating.
Residue *B*	5·0	0·05	0·28	0·40
90% res. *B* + 10% gas oil	4·5	0·13	0·38	0·74
70% „ + 30% „	3·9	0·20	0·53	2·20
50% „ + 50% „	3·3	0·71	1·11	2·50
30% „ + 70% „	2·5	1·01	2·1	3·40
10% „ + 90% „	0·8	0·63	0·54	0·59

* During heating the products were placed in closed one-gallon tins. Heating to 100° C. was effected in a drying oven.

The relation between the increases in B.S. & W. with the sludge content is given in Fig. 27.

In Table IX and Fig. 28 similar data are collected referring to residue *C* and the dilutions of *C* with gas oil.

TABLE IX.

Product.	Sludge Content, %.	B.S. & W.		
		Before Heating.	After 5 Days' Heating.	After 10 Days' Heating.
Residue *C*	7·4	0·30	0·30	0·35
90% res. *C* + 10% gas oil	6·1	0·26	3·5	5·6
70% „ + 30% „	4·6	0·20	4·7	6·0
50% „ + 50% „	3·2	0·58	5·3	6·0
30% „ + 70% „	2·1	1·95	3·8	4·8
10% „ + 90% „	0·8	1·70	1·5	2·0

It may be seen from the data that there is no relation between the sludge contents and the heating stability. In both examples the sludge content of 100 per cent. of residue to plain gas oil diminishes regularly. The instability upon heating has a clearly marked *maximum*: in the case of residue *B* and its mixtures the maximum instability upon heating is with a

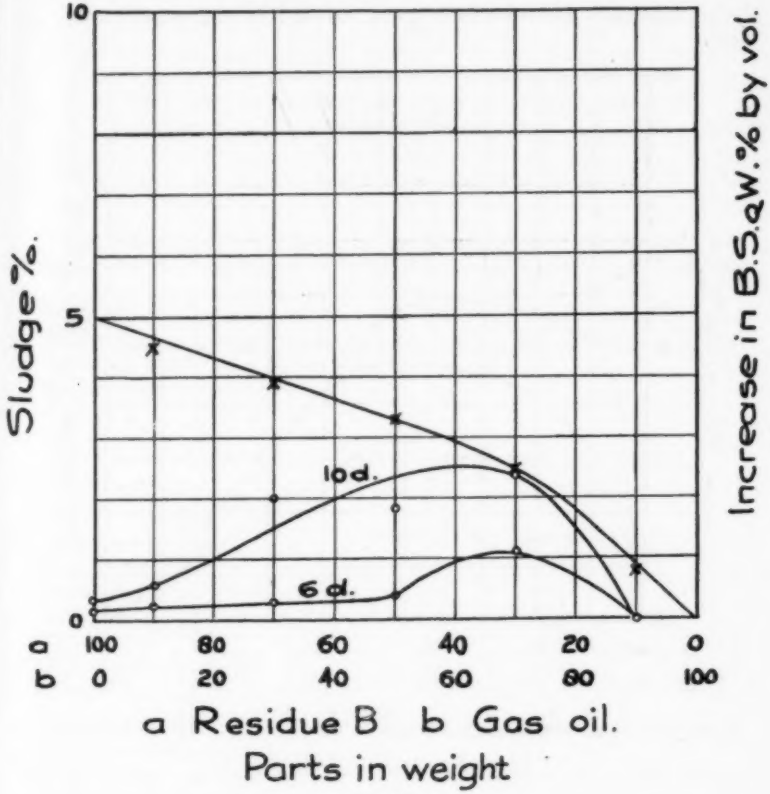

FIG. 27.

RELATION BETWEEN SLUDGE CONTENTS (×) OF RESIDUE B AND MIXTURES OF THIS AND GAS OIL, WITH THE INCREASES IN B.S. & W. (○) AFTER 6 AND 10 DAYS' HEATING, RESPECTIVELY, AT 100° C., OF THE RESIDUE AND THE MIXTURES.

mixture consisting of about 30 parts by weight of residue and 70 parts by weight of gas oil, and in the case of residue *C* and its mixtures with about 55 parts by weight of residue and 45 parts by weight of gas oil.

What is the cause of there being no relation between the sludge content and the heating stability? In order to be able to answer this question, we must consider *the influence of the medium* on the sludge. When discussing the working hypothesis which tried to explain the construction of cracked

residues, it was already stated that if the part of the medium that keeps the sludge in dispersion has not become too small, flocculation of the sludge is still reversible. This reversibility, however, constantly diminished if a gas oil is added, as the sludge can continually adsorb less and less dispersion medium. The sludge, therefore, becomes more and more "isolated," and the consequence is that an *external* factor, *oxygen*, is able to affect the sludge, making it insoluble in benzene, as the following experiments will show.

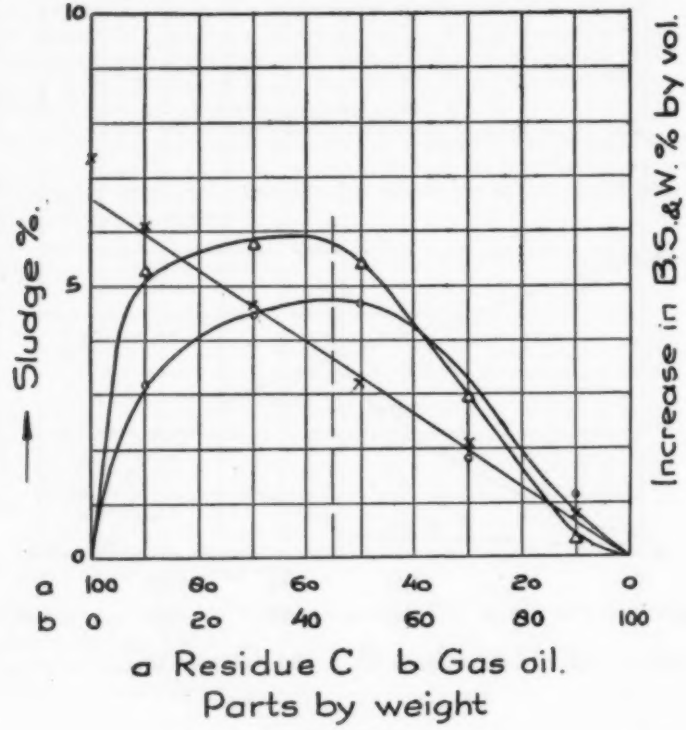

FIG. 28.

RELATION BETWEEN THE SLUDGE CONTENTS (×) OF RESIDUE C AND MIXTURES OF THIS AND GAS OIL, WITH THE INCREASE IN B.S. & W. (○, △) AFTER 6 AND 10 DAYS' HEATING, RESPECTIVELY, AT 100° C., OF THE RESIDUE AND THE MIXTURES.

1. Flash fuel *P* (sludge content 1·5 per cent.) and a mixture of this flash fuel with three parts of cracked gas oil (sludge content 3·5 per cent.) in gum stability bottles were plunged into boiling water and the B.S. & W. content determined before and after heating for 15 hours.

In one bottle the fuel was contained in an atmosphere of O_2 and in the second and third bottles in H_2 and CO_2, respectively. Results are given in Table X.

TABLE X.

Atmosphere.	B.S. & W.	
	Before Heating, %.	After Heating, %.
(50 ml. of flash fuel *P*, sludge content 1·5%.)		
O_2	0·8	0·9
H_2	0·8	0·9
CO_2	0·8	0·9
(50 ml. of blend consisting of 1 part of flash fuel *P* and 3 parts of cracked gas oil.)		
O_2	0·3	4·7
H_2	0·3	1·6
CO_2	0·3	1·7

2. The assumption that the oxidizable component of cracked fuels consists mainly of unprotected, isolated sludge, is supported by the following test.

0·5 Kg. of several mixtures of flash fuel *P* and gas oil were placed in flasks to which reflux condensers were attached, and for three hours a moderate current of air at 140° C. was conducted in.

The results are given in Table XI.

TABLE XI.

Mixture.	Sludge Content, %.	B.S. & W.	
		Before Heating.	After Heating.
1 part flash fuel *P* + 0 gas oil . .	1·5	0·8	0·9
1 „ „ + 0·5 „ . .	1·9	0·4	0·8
1 „ „ + 1·0 „ . .	1·8	0·4	3·5
1 „ „ + 2·0 „ . .	1·3	0·7	8·0
1 „ „ + 3·0 „ . .	1·1	1·0	12·0

The sludge in the undiluted flash fuel still contains sufficient dispersing medium to be protected against oxygen.

The same may be said of the 1 : 0·5 dilution, although in this case a maximum sludge content was shown.

With increasing gas oil dilution the sludge becomes more and more isolated, and larger and larger quantities can be attacked by the oxygen and made insoluble in benzene.

It is known from the literature on the subject that isolated asphaltenes are the most seriously subject to oxidation, being converted to carboid-like bodies.[2]

The increase in carboid-like bodies as a result of oxidation of the medium may be disregarded here, as the conversion takes place via asphaltene formation, therefore passes through several stages and, moreover, is effected at a much slower rate.

If, finally, it is kept in mind that oxygen easily dissolves in oil products,

and the presence of metal surfaces catalytically accelerates oxidation of the oil products, it is easy to understand that under certain conditions heater sludge can be formed very rapidly in preheaters.

The writers have not yet studied those cases in which heater-coating occurs in the *absence* of sludge. Such cases do occur in practice. From tentative tests made, the following explanation may be given, provisionally. The medium has sufficient solvent capacity to keep the components with the highest C : H ratio in solution in the fuel. If this fuel flows through the heated tubes into the preheater, the lightest constituents in the medium are converted into vapour immediately round the tube, and this vapour soon condenses in the cooler layers of the fuel. Therefore, local accumulations of this light constituent are formed. This excess probably flocculates sludge. If the temperature is now high, if there is much oxygen present, or if the medium is at the limit of its solvent capacity, the flocculated sludge is immediately converted into heater sludge.

The authors wish to express their thanks to the Management of the Bataafsche Petroleum Maatschappij for their kind permission to publish the foregoing.

Laboratory,
N.V. De Bataafsche Petroleum Maatschappij,
Amsterdam.

Laboratory,
Astra Romana, Ploesti.

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THE STRUCTURE OF LUBRICATING GREASES.*

By A. S. C. Lawrence, Ph.D.

Summary.

Soap–oil systems exist in three forms: true solution, true gel and pseudo-gel, which is a paste of micro-crystals. Commercial lubricating greases may be in stage 2 or 3. There is a well-defined temperature of transition from 2 to 3 which depends on the nature of the soap used and upon the presence of polar substances, such as fatty acid, water or glycerin, which lower it. These greases are not emulsions. Natural greases such as butter and tallow are emulsions in which the dispersion medium is a soft solid. Dispersion of the soap in the oil can be brought about by stirring at any temperature above that of the transition and does not require raising to that of true solution. Formation of gel and pseudo-gel are crystallizations and the mechanical properties of the systems are due to the peculiar crystal habit and properties of the separating soap particles. The properties are profoundly modified by small amounts of fatty acid.

The name "grease" was originally applied to substances such as butter and tallow. Being taken to mean any soft solid or semi-solid with lubricating properties, it was extended to cover the thickened paraffin oils. It is now necessary, therefore, to recognize under the title several types with different structure and mechanical properties.

1. Soft crystalline substances such as the fats. These have low melting points.

2. Two phase solid–liquid systems such as butter which is an emulsion of liquid water dispersed in solid fat. The disperse phase is in spherical droplets or polyhedra according to the concentration.

3. Thickened oils which may be :—

(*a*) one-phase stable gels or liquids of very high viscosity.
(*b*) two-phase suspensions of anisodimensional soap crystallites.

This paper is concerned only with class 3.

Lubricating greases, consisting of mineral oils thickened by soaps of sodium, calcium, aluminium and lead, are used largely for a number of diverse purposes.[1] Papers have appeared on the metallic soaps and their thickening action;[2] and an excellent account of the manufacture of lubricating greases has been published by Garlick.[3] Nevertheless there is no information published on the physical chemistry of these curious systems. The question, What is a grease? is answered, A water in oil emulsion stabilized by soap or, more vaguely, a colloidal solution of soap in oil. No evidence is cited in favour of these statements, which are, in fact, entirely untrue. In other words, we have no (published) knowledge of the value of greases for the particular purposes to which they are applied, nor of their limitations, nor of their optimum composition for such uses. Knowledge of the best methods for manufacture of greases is the result of

* Paper received December 29th, 1937.

experience, and is not based on any fundamental knowledge of the results to be aimed at. Our ignorance of these points is clearly emphasized by the discussion which followed Mr. Garlick's paper. Work on non-aqueous gels, published in full elsewhere and summarized here, throws considerable light upon the nature of greases and on the actual problems which they present.

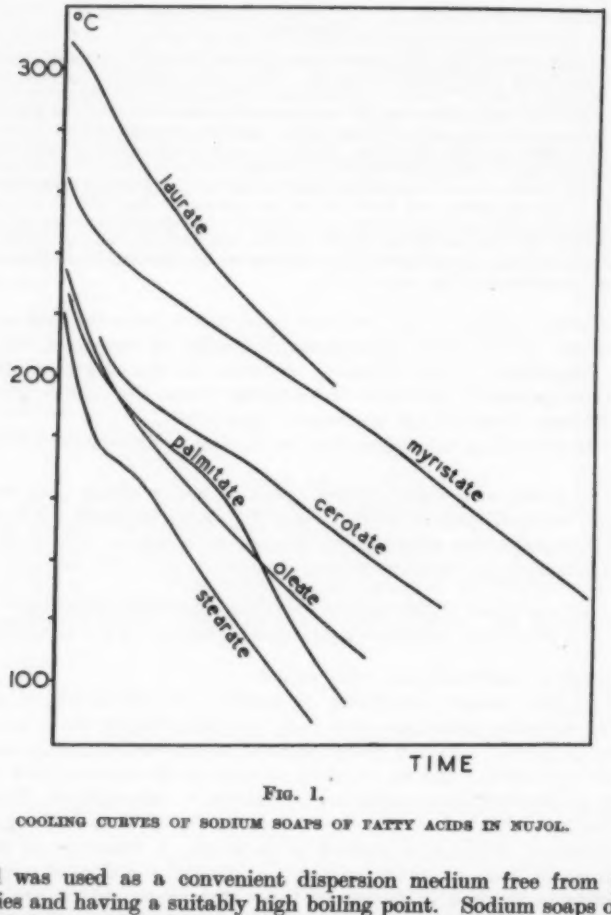


FIG. 1.

COOLING CURVES OF SODIUM SOAPS OF FATTY ACIDS IN NUJOL.

Nujol was used as a convenient dispersion medium free from polar impurities and having a suitably high boiling point. Sodium soaps of the saturated fatty acid homologous series were examined first. Below the laurate—C 12—they are insoluble up to the boiling point—*c.* 340° C. The higher members, when heated with nujol, swell somewhat at first and then, at a temperature in the neighbourhood of 200° C., dissolve suddenly to a clear mobile liquid. On cooling, this sets to a clear gel slightly below the dispersion temperature, T_1. On further cooling to T_2, the gel becomes

opaque and its mechanical properties change markedly. It becomes harder but less elastic, and is no longer homogeneous. There is considerable syneresis and extrusion of oil. If the solutions examined are sufficiently dilute—of the order of 0·1 per cent., segregation of the soap as a microcrystalline deposit occurs below T_2.

Fig. 1 shows the gelation temperatures, determined by cooling curves, plotted against the number of carbon atoms in the soap molecule. 1 per cent. solutions were used, but the setting point does not increase until the soap content is more than 20 per cent. The laurate is peculiar in that it separates from the nujol as a liquid which, at a lower temperature, solidifies. No gel is therefore formed. It is clear from Fig. 1 that the hydrocarbon chain needs to be a certain length for solution to occur. C_{11} in the laurate is just enough for solution a few degrees below the boiling point of nujol. The greater solvent action of the oil on the hydrocarbon chains of the soap shows itself in the higher members of the series as lower gelating temperatures.*

Table I shows the results for the sodium soaps, including some of those of the unsaturated and substituted fatty acids. These figures apply to the monohydrated soaps (see p. 216).

TABLE I.

Fatty Acid.	Nujol Solution.		Soap Alone.	
	Gelation T_1.	Transition T_2.	M. p.	Trs.
Acetate	Insoluble up to b. p.		—	—
Valerate	,,	,,	220	—
Caprylate	,,	,,	345	217
Pelargonate	,,	,,	250	—
Laurate	337 (liq.)	240 (solid)	324	200
Myristate	206	180	312	205
Palmitate	223	125	291	150
Stearate	207	139	291	163
Arachidate	175	140	—	—
Cerotate	153	122	360	108
Oleate	226	*c.* 100	245	140
Elaidate	—	—	280	120
Stearolate	280	—	—	—
Linoleate	Insoluble up to b. p.		—	—
Ricinoleate	—	—	215	175
Cetylsulphonate	No gelation.			
Dioctadecylacetic	,,			
Dioctadecylmalonic	,,			
Mono-octadecylmalonic	,,			

The effect of varying the cation was then examined. Stearates and cerotates of the alkali metals and stearates of a number of metals were prepared and tested in nujol. Some formed gels and some did not. Table II shows the results.

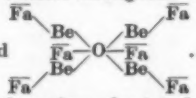
* Some grease-makers seem to believe that m. p. of grease is parallel to that of fatty acid, whereas we see that the reverse is true.

TABLE II.

Gelating Stearate of:	Nujol Solution.		Soap Alone.	
	Gelation T_1.	Transition T_2.	M. p.	Trs.
Sodium	207	140	291	163
Potassium	224	130	270	138
Rubidium	258	82	360	185
Cæsium	235	—	340	105
Silver	127	45	—	—
Aluminium *	—	50	280	90
Calcium	270	—	—	—
Magnesium	—	40	240	109
Nickel	—	—	240	below 15
Cobalt	60	4	200	"
Manganese	—	—	*c.* 200	80
Copper	—	—	111	80
Uranyl	—	—	82·5	*c.* 70
Ferric		Readily soluble at 15°.		

	Non-Gelating and Non-Plastic Soaps.	
	M. p.	Transition Point for Dimorphous Salts.
Li	136	78
NH_4	107	50
Tl	163	128 (to smectic)
Pb	106	—
Hg	117·5	—
Th	73	—
Be †	35	—
Zn	118	—

* Only the monosalt $AlO\overline{Fa}$ exists throughout the fatty acid series.

† Co-ordination compound  . In the crystalline acetate, the four beryllium atoms lie at the apices of a tetrahedron, the centre of which is the oxygen.[4]

It was noticed that the strength of gel was parallel to the hardness of the soap. For example, cobalt stearate is of pitch-like consistency, nickel oleate approximates to the consistency of commercial water glass, nickel stearate is intermediate. 2 per cent. nickel oleate forms a gel the strength of which is insufficient for it to be self-supporting; that of nickel stearate is just self-supporting, and that of cobalt stearate is tougher still. It was then found that the apparently random appearance of the phenomenon of gelation in nujol solution is parallel to the physical state of the soap. Only those soaps which, on heating, pass through an intermediate plastic form, which at a higher temperature, melts sharply to isotropic liquid, gelate in oil solution. Further, the range of stability of gel, T_1 to T_2, is parallel to the temperature range over which the solid soap is plastic.

Fig. 2 shows the results for the sodium soaps of the saturated fatty acid series and Fig. 3 for the cerotates of the alkali metals.

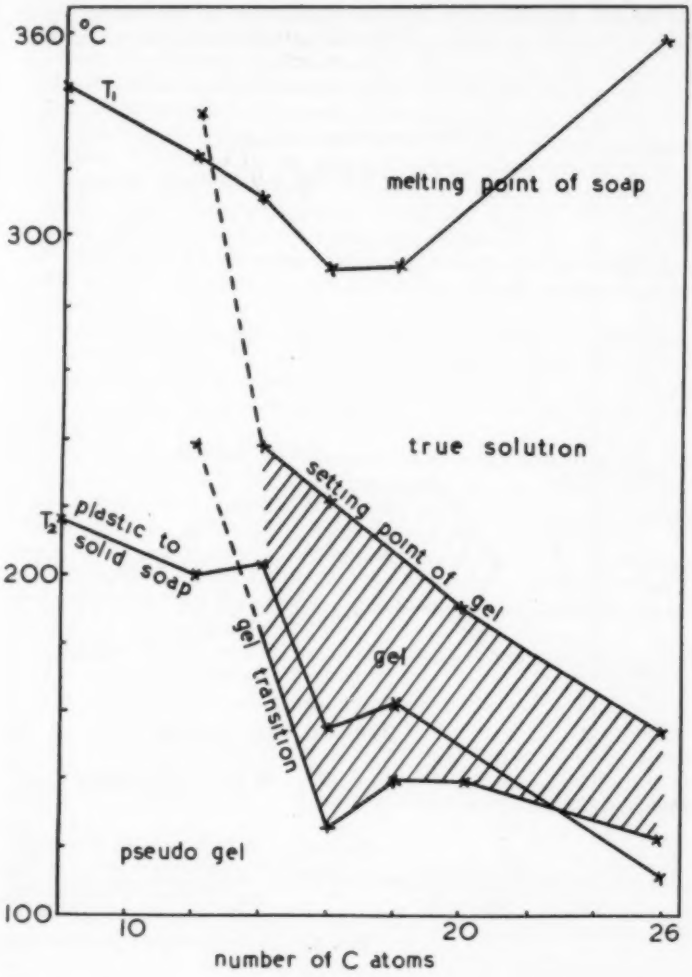


FIG. 2.

It is clear now what is happening. On heating the soap with nujol, the oil can penetrate only in between the hydrocarbon chains of the soap crystal lattice. Solution occurs when the temperature is high enough for thermal disruption of the polar $-CO_2Na$ groups. This occurs somewhat below the actual melting point of the solid soap, because the thermal

oscillations of the hydrocarbon chains * of the soap molecules help to disrupt the polar groups. This reduction of adhesion of the polar groups will increase with length of hydrocarbon chain, but the temperature required for corresponding thermal oscillation of the chains increases regularly with chain length. The melting point in the homologous series

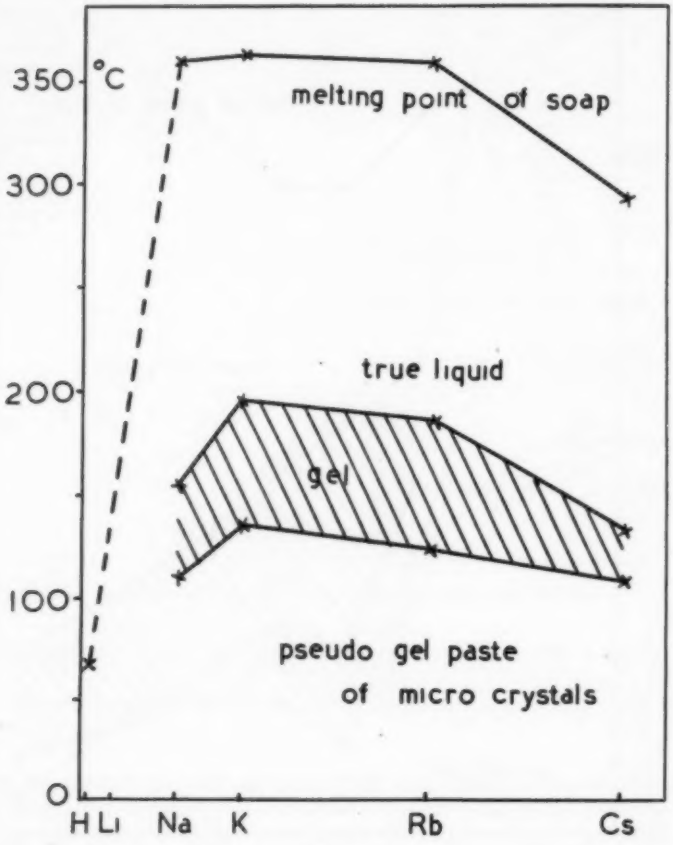


FIG. 3.

therefore falls at first as the chain length increases, and then in the higher members rises again slowly. In solution, the hydrocarbon chains are in potential solution, and all homologous soaps are in corresponding state at a given temperature. The solution temperature therefore falls continuously with increase of chain length.

* Melting points are above boiling points of hydrocarbons of same chain length.

Gelation is therefore a crystallization. The soap separates suddenly and in a peculiar crystal habit, so that a meshwork is formed holding the oil like a sponge. There are two reasons why the stable gel is formed only by those soaps which pass through the plastic stage. First, those soaps which do not pass through the plastic stage all have low melting points which increase with increase of chain, thus showing that the adhesion of the hydrocarbon chains is greater than that of the polar heads. And secondly, the plastic state of the soap is, in the gel structure, swollen with oil and unable to undergo particle growth according to the thermodynamical considerations which make a suspension of small crystals unstable.

The dispersion temperatures of the oleates are much the same as those of the stearates, as would be expected on the above view. Their crystallizing temperatures, however, are considerably lower.

Soap–oil systems can therefore exist in the following three forms :—

1. True solution the viscosity of which is but slightly greater than that of the oil alone.

2. True gel—that is, a stable transparent, homogeneous elastic system. If the concentration of the soap is too low for formation of a gel self-supporting under gravity, a solution with anomalous viscosity is formed. The elasticity may become vanishingly small, but the viscosity is very large (see p. 217).

3. Pseudo-gel or paste of fully crystalline soap suspended in oil. The crystallites are very tiny, but grow larger on standing. With sufficient concentration of soap the system is a plastic paste, *i.e.* it has a yield point due to its rigidity. At small concentrations the soap segregates. The system is not homogeneous, distortion of the paste produces artefracts which do not "heal." Contraction of the soap in the mixture, either by thermal contraction or by particle growth, causes extrusion of oil and "bleeding."

We may note that in certain soap–oil systems, T_2 is below room temperature, *e.g.* for cobalt stearate T_2 is 4° C.

We now have the following points to consider in a grease :—

1. In which physical state do we require our grease to be for a specific purpose—gel or paste?
2. What is the best soap and the best concentration for a specific purpose?
3. Optimum temperature for preparation.
4. Effect of added polar substances such as water, glycerine and fatty acid, on the above points.
5. Correlation of other physical characteristics of greases with their composition and value as lubricants.

1. We cannot state that all greases should be gels or that all should be pastes. Soda and aluminium base greases are certainly paste type, and lime base is probably gel. The effects of calcium soaps need further attention, owing to the number of foreign polar substances which are associated with them in grease and because they are not well-defined systems even when pure. Preliminary experiments suggest that when mixtures of soaps are dissolved in nujol, the resulting mechanical properties

are far from additive.* Greases cover a wide range of types. This would make them especially valuable if it could be decided once and for all what lubricating conditions require each particular type. Measurements have been reported of static friction of greases,[5] but this method seems to be of doubtful value for assessing lubricating efficiency, since the results depend on the internal cohesion of the grease as well as, or more so than, lubricating value.

2. The choice of a soap as thickener involves two factors: the temperature range of rigidity desired, and again the unknown point of the most suitable physical state. Grease structure will prevent free flow of lubricant required for efficient lubrication.† This is avoided in practice by pressure feeding. If the temperature of the bearing is high enough, the grease will be fluid in the parts where it is needed. The value of T_1 of a grease may therefore be a guide.

The concentration of soap used in greases is high—15 to 20 per cent. With increase of concentration of soap, the hardness of the grease at ordinary temperature increases, and at all temperatures below T_1 the difficulty of supplying it to a bearing increases. How far the value of a grease for film lubrication increases with soap content is doubtful, since the film strength depends as much upon the physical properties of the individual fibrils in the grease as upon their number. High concentrations of soap prevent "bleeding." When syneresis occurs on cooling, the matter which separates is soap swollen by oil included among the hydrocarbon chains of the soap molecules. Knowing the amount held in this way, it is a simple calculation to find the minimum concentration of soap required to retain all the solvent oil. 1 gm. of calcium stearate retains 4·7 c.c. of nujol. 17·5 per cent. of soap is therefore required to prevent "bleeding." The absorption of oil by soaps on heating is not a solvent action by the oil, since the soaps alone expand to a remarkable extent. The density of sodium stearate is only 0·4 at its melting point. As the soap lattice opens up, oil enters between the hydrocarbon chains. The amount of syneresis therefore depends on the difference between the dispersion and room temperature.

3. The temperature of preparation of a grease should be as low as possible, to prevent syneresis. Grease-makers like to work below T_1, since paste-type greases formed from gel by internal phase change are liable to be less homogeneous than if mixed between T_1 and T_2. For dispersion, the temperature must be above T_2, high enough for easy mechanical agitation but as low as possible to reduce syneresis on cooling.

4. Recognition of the need for the presence of small amounts of water, glycerine and fatty acid has given rise to the myth that greases are emulsions of water in oil stabilized by the soap. It is only necessary to point out that greases have none of the characteristics of emulsions, and that

* Analysis of a metal base grease should include estimation of soluble ash. Metal soaps prepared by metathesis always retain alkali soap which affects the behaviour of the metal soap in oil.

† The practice of working grease before making tests of its mechanical properties is of little value when tests are not also made on the unworked grease. For continuous use, the worked test is obviously more valuable, but for discontinuous use, the unworked test is wanted. Generally, high unworked and low-worked values would seem to be most desirable for economy in use and efficiency in lubricating.

there is a simple mechanism which, in the light of the work described here and elsewhere by the writer, accounts for all the observed facts. Polar substances in small quantity aid dispersion and alter the nature of the grease. It has been shown in previous papers that aqueous soap solutions are peptized very efficiently by small amounts of alcohols, phenols and amines.[6] Sugars, including glycerine, peptize, but much larger amounts are required, since there is a distribution of the added

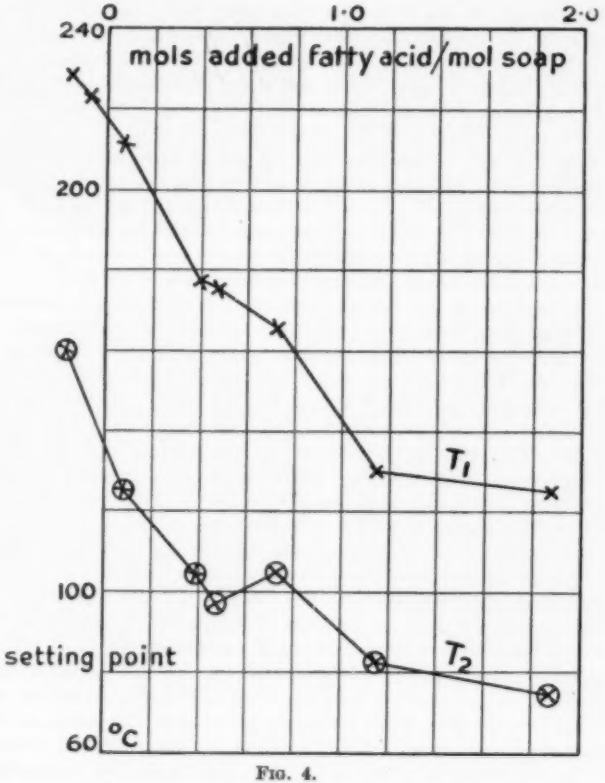


FIG. 4.

SODIUM STEARATE + STEARIC ACID IN NUJOL.

substance between solvent and soap. It was suggested that the mechanism of the attachment of the added polar substance is dipole adhesion to the polar groups of the soap, thereby reducing their mutual cohesion. There is a definite saturation value for all peptizers partly miscible with water. It is not possible to determine directly with the necessary accuracy the amount of water taken up by sodium and calcium soaps dissolved in nujol, since the determination needs to be carried out at 200° for the former and higher for the latter. Glycerine is quite suitable, since it

does not dissolve in the nujol, and direct determinations of the solubilty in 10 per cent. solution of sodium stearate in nujol were made. The solubility was 68 gm. of glycerine per 100 of soap. The setting point to gel was lowered to 140° and the transition to 88°. The texture at room temperature was changed, and the mixture was a structure of fine silky fibrils. Preliminary estimations of the solubility of glycerine in calcium stearate in nujol were made, and showed a similar saturation. When greases are made from glycerides and alkali in the oil, the amount of glycerine is about 10 per cent. of the soap (Ca and Na). The value was found to increase considerably with small amounts of fatty acid. It is curious that the importance of free fatty acid has been so largely ignored in the work published, since it has marked effects both alone and in the quaternary systems containing polar substances. This is all the more remarkable since commercial specimens of soaps examined contained large amounts of free fatty acid. To neutral anhydrous calcium stearate in nujol, increasing amounts of stearic acid were added until equimolecular proportions were reached. T_1 falls progressively, and so does the rigidity of the mixture. In the sodium stearate–stearic acid–nujol system, T_1, T_2, and the elasticity all fell on addition of stearic acid, steeply at first and becoming asymptotic above the equimolecular ratio (Fig. 4).

The effect of water on sodium stearate was determined indirectly by preparation of anhydrous soap from fatty acid and clean sodium. When dissolved in nujol, no gelation occurred. A minimum of 1 mol. of water of solvation was required, *i.e. c.* 6 per cent.* When more polar substance is present, it is apt to cause crystal growth in stage 3, so that the particles of soap become objectionably large (Figs. 5 and 6). Less polar substances, such as the glycerides, are used largely in practice. They give the grease a smoother texture. The greases formed from less-purified oils tend to be smoother than those from more highly refined ones. Presumably this is due to slightly polar impurities present. In this connection it may be noted that diphenylmethane has a marked peptizing effect in greases when present in fairly large amounts—*c.* 20 per cent.

Observations of calcium stearate and its paraffin dispersions have shown that the fatty acids have a powerful effect on the soap. The evidence suggests the formation of complexes of the formula: $Ca(St)_2 : H\overline{Fa}$ where $\overline{Fa}$ may be any fatty acid. These complexes are more soluble than the neutral soap. There is no interchange between acids added as peptizer and the calcium stearate when the latter crystallizes the peptized solution. Water, glycerol and glycol act as peptizers by the hydrolysis which they cause. In the presence of excess of lime, they have no peptizing effect. The clearing temperature of nujol solutions of the calcium stearate/fatty acid complexes is a linear function of the chain length of the added acid, rising from 47° for acetic to 118° for stearic.

5. Before statements can be made on the optimum composition and nature of greases, it is necessary to specify first the duty for which they

* Soda soap greases are said to possess the capacity for taking up water by emulsification, and so protecting iron from rusting. Lime base soaps do not possess this property. Since calcium soaps are very much better emulsifiers of water-in-oil than are soda soaps, this explanation is suspect. A more probable one is that the protection is due to Na ions hydrolyzed out of the grease.

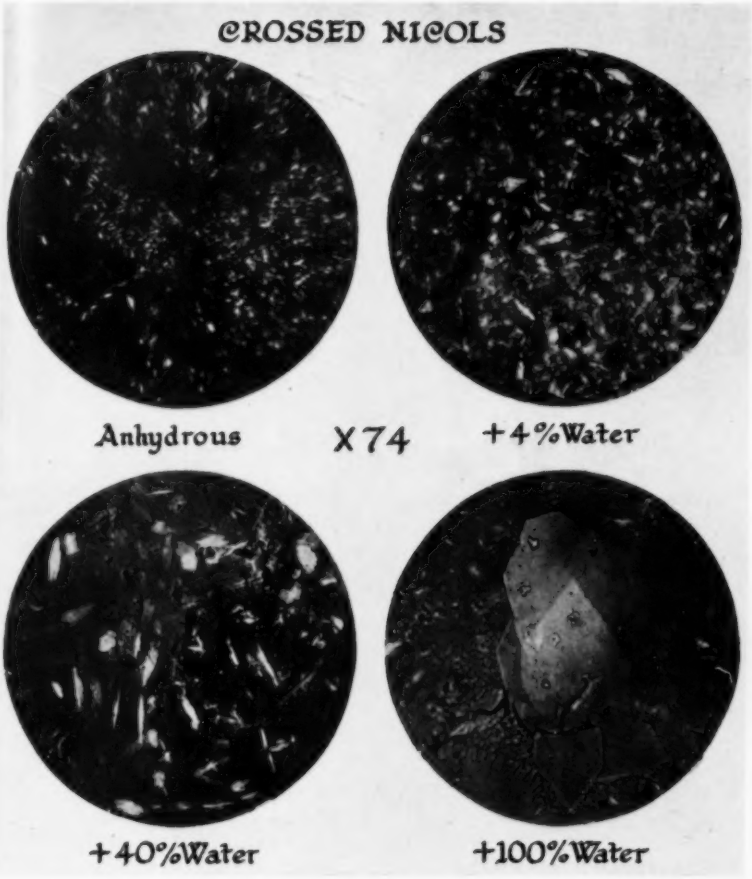


FIG. 5.

EFFECT OF WATER ON PARTICLE SIZE IN GELS OF SODIUM STEARATE IN NUJOL.

N.B.—The magnifications stated are those given in the original microphotographs of the Author. The above plates have been reduced to approximately two-thirds of their original size.

[*To face p.* 216.

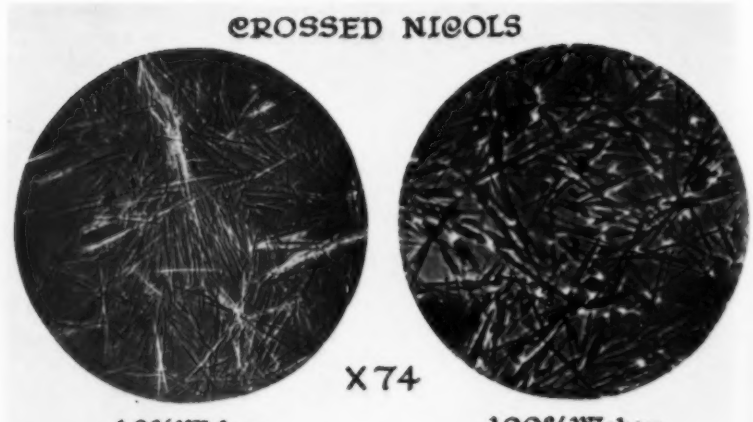


FIG. 6.

EFFECT OF WATER ON PARTICLE SIZE IN GELS OF SODIUM STEARATE IN NUJOL.

N.B.—The magnifications stated are those given in the original microphotographs of the Author. The above plates have been reduced to approximately two-thirds of their original size.

are required. We are immediately faced with one serious difficulty. Are greases only to be regarded as preferable to the oils from which they are compounded for their advantages in application? Or are greases superior lubricants to the oils? It has been claimed that greases retain their body at elevated temperatures, and so give more efficient lubrication under these conditions. This claim has not been substantiated by evidence, and appears to be most unlikely in view of the melting points attainable by greases and the high local temperatures existing at the surfaces to be lubricated.[7] As temperature and rate of shear increase, the behaviour of a grease approaches that of the oil from which it is made. Its body is at a maximum at smallest rates of shear. This makes greases valuable for lubricants where economy is important, since they do not flow under gravity, but do so in a bearing, provided they are supplied adequately.

Examination of the mechanical properties of greases is obviously important, especially their temperature changes. Calcium soaps have higher T_1 than sodium soaps. They are considered to be more heat resistant. The actual value of T_1 is the temperature at which the system becomes liquid. It gives no information of the rate of increase of "body" at temperatures below.

Fig. 7 gives a picture of the variation of mechanical properties of greases with temperature. It is idealized, in that a single stress value is considered, whereas their resistance to flow varies with the rate of shear, and a family of curves is needed for each substance and each concentration. On cooling a solution of a substance which undergoes a phase change at T_2 from plastic to rigid crystalline, its apparent viscosity will increase abruptly at this temperature and $d\eta/ds$ will be steeper below T_2. What actually happens is quite different, because the phase change includes particle growth. Above T_2, therefore, the number of particles is considerably larger. The apparent viscosity therefore rises sharply, and $d\eta/ds$ is larger just above T_2, although with further rise of temperature the system begins to lose its "body" more rapidly as it approaches T_1. The distance between T_2 and T_1 depends on the soap used. For lead soaps it is very small, for sodium soaps about 80° and for calcium stearate *c.* 300°.

Finally, it must be noted that systems are frequently classified as gels without consideration of the meaning of the word "gel." It describes elastic bodies. The simple test of retention of shape under the deforming force of gravity is quite inconclusive, since a liquid of sufficiently high viscosity behaves to this test over a small time interval as a gel. That is, it flows slightly, but the flow is so small that it cannot be observed without very accurate measurement. A solution of 5 per cent. magnesium oleate in nujol has a viscosity of 10^{10} that of water. It is a liquid, but appears to be a gel. The point is of practical importance to the feed problem.

The resistance to flow in Fig. 7 is due to viscosity plus rigidity or plasticity. The anomalous flow of greases makes all methods of testing, which depend on flow suspect. The nature of the velocity gradient in the specimen under shear is quite unknown, highly complex and different in different tests. Extensive wall-slip and plug flow occur in paste type greases, while the gel type also give different values as the rate of shear is altered.

Arveson [8] has made measurements of the apparent viscosity over a wide range of rates of shear. The general form of the η_a–shear curves is a

flattened inverted S. Having thus proved the flow to be anomalous, analysis of the results is made by transformation of the Poiseuille equation as follows :

$$\eta_a = \frac{PR^4t}{8LV} = \frac{\frac{PR}{2L}}{\frac{4V}{tR^3}} = \frac{F}{S}$$

where F is the force applied, S the rate of shear, and η_a the apparent viscosity.

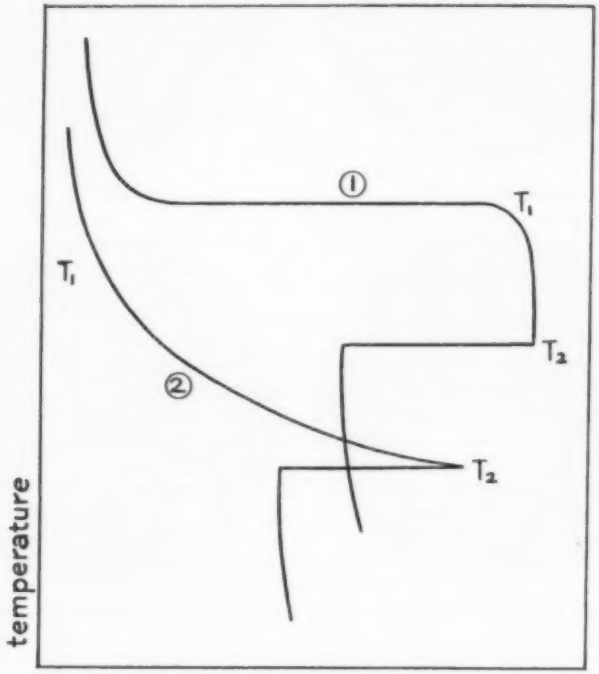


FIG. 7.

CURVE (1) ALKALI SOAPS.
CURVE (2) SOAPS OF Co, Ca, Al, Mg ETC.

This procedure is very misleading. It is clear that we are dealing with three different types of flow. At high rates of flow, resistance is falling towards that of the unthickened oil. The grease structure is broken down. At intermediate rates, the high apparent viscosity is due to part of the applied force being used up in breaking down the grease structure. The falling off of the increase of apparent viscosity with decrease of rate

of flow at low rates suggests "plug" flow; *i.e.* the grease is moving through the tube as a solid plug lubricated by a thin anulus in which the rate of shear is large. Such behaviour has been observed in clay pastes. In this case, the anulus may be richer in oil than the grease owing to syneresis of the grease structure. Aluminium soap greases did not show this falling-off effect at low rates of flow, but I have found aluminium stearate in nujol to form a thixotropic suspension at room temperature. Its resistance to flow is slight above its yield point.

The fundamental objection to all flow experiments is that they involve a parabolic velocity distribution across the tube if flow is Newtonian. The observed flow is therefore the sum of flows at rates of shear differing greatly according to the distance from the wall of the tube. The velocity distribution is unknown in anomalous flow and very complex. The complexity varies with the nature of the system and the conditions of flow.[9] The Poiseuille equation assumes parabolic velocity distribution. Arveson suggests that the lime soap greases consist of "interlacing flexible solid members, which may be themselves deformed or merely separated by the shearing action." He explains the immediate return to worked consistency from the highly sheared state on emerging from the tube by elastic recoil. This explanation is not complete. Interlacing confers no rigidity on the system unless there is adhesion at the points of contact. Stretching by shear also involves orientation along the stream lines. When the stretched particle reaches this position, there is no longer any force stretching it, and it will contract, and remain so until it is displaced across the velocity gradient by Brownian motion. It seems probable that the system has some rigidity. Working consists of breaking lumps of gel into a homogeneous mixture. Shearing then progressively breaks down the adhesion of the crystallites. On removal of the shearing force, adhesion occurs immediately at the points of contact by van der Waals forces.

These points could be decided easily by examination of the diluted grease in a coaxial cylinder viscometer. It may be noted, however, that the crystal habit of the metal soaps is elongated plates with a length/breadth ratio of about 5 to 10. Calcium stearate gives progressively smaller plates on addition of peptizers such as stearic acid and water, but the shape as seen in polarized light is similar. The most accurate results are obtained by diluting the grease with inert dispersion medium such as nujol until the concentration is 0·1 per cent. or less. The homogeneity of the grease is then easily observed, and its mechanical properties—apparent viscosity at different rates of shear and rigidity—can be observed in the coaxial cylinder type of viscometer. In any case, it is obvious that the temperature changes of constitution and properties are even more important than the value determined at any particular temperature.

At present most of the information published about greases concerns their preparation. It seems that the only hope of rationalizing the subject lies in systematic examination of the physical properties of simple systems and comparison with performance under various conditions, and then in finding the effects on these properties of added polar substances. The effects of impurities in the oils can then be deduced in terms of their polarity, even if their actual nature is unknown. Only in this way can

we discover what degree of complexity of composition of a grease is desirable for any particular performance. If this preliminary work were carried out properly, the value of any sample of commercial grease could be assessed by a few simple chemical and physical tests.

One of the peculiar advantages of greases is the wide range of properties and behaviour which can be realized, and which should make it possible to compound the best grease for any given job. In the paste-type, the shape and hardness of the crystallites will determine the properties, and an interesting attempt has been made to correlate these by dark-field microscopic examination of the grease. It was found that the "shortness" of the grease was proportional to the length and size of the particles in the grease.[5] Such a method, however, can reach its full value only when the performance of the grease as a lubricant is also correlated with these two other properties.

In the discussion which followed Mr. Garlick's paper, it was suggested that it was desirable that a University Department should take up the problem of greases. This paper is a beginning. Obviously considerable further work is required, especially on the effects of added polar substances. Complete examination of the anomalous viscous properties of these systems is also needed. The author considers that this paper does, however, provide a fairly complete and accurate picture of the nature of greases, of their states and of the lines of further research which are likely to prove profitable. The work described forms part of certain investigations undertaken for the Fuel Research Division of the Department of Scientific and Industrial Research. It was carried out in the Laboratory of Colloid Science, Cambridge, by kind permission of Professor E. K. Rideal to whom the author is grateful for encouraging and helpful advice.

Laboratory of Colloid Science,
Cambridge.

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CATALYSTS IN HYDROCARBON CHEMISTRY.*

By E. K. Rideal, F.R.S.

Synopsis.

In hydrocarbon chemistry increasing attention is being paid to catalytic processes. It is shown that these can be formulated on a radical mechanism. Homogeneous reactions can be brought about by free radicals and heterogeneous reactions by chemi-adsorbed radicals. The energy of activation of such heterogeneous processes is less than one-fourth of the corresponding homogeneous reactions. This permits of lower temperature operation, greater efficiency and greater control. The use of *o. p.* hydrogen and of deuterium as tools for the elucidation of the mechanism of hydrogenation is briefly indicated.

Natural hydrocarbons are being utilized in increasing quantities as raw materials for conversion into other products more suitable for special purposes. The products include not only derivatives such as the sulphonic acids and alcohols for textile and related industries, unsaturated hydrocarbons for the plastic and rubber industries, phenoloids for disinfectants and varnishes, but we must also consider the growing consumption of manufactured fuels and lubricants synthesized from hydrocarbons. The changes to be effected in hydrocarbons themselves must include chain extension and fission, ring closure and opening, conversion of straight into branched chains, introduction of one or more double bonds and the like. In many of these transformations free radicals are concerned, and it is of some interest to examine under what conditions free radicals may play a predominant part in such reactions.

Since the energy required for breaking a C–C or C–H bond in a hydrocarbon is relatively great, being *ca.* 95 kg.-cal. per gm.-mol., it is evident that homogeneous chemical reactions involving the production of free radicals cannot take place except at somewhat elevated temperatures—in fact, well over 600° C. Such high-temperature reactions are not only uneconomic in themselves, but the great variety of reactions which can take place in a long hydrocarbon chain when rupture does occur preclude one from obtaining high yields of any one particular product except under very limited conditions of operation. In order to arrive at some understanding of the processes at work in heat treatment of hydrocarbons, it is evidently necessary to determine what in fact are the modes of decomposition of hydrocarbons, *i.e.*, what free radicals or other products are formed, whether the reactions are of low order or whether chain reactions intrude, and then to study the reactions which these free radicals can undergo both with the original hydrocarbons and with the other products of thermal decomposition. We can then devise various methods for the production of specific free radicals, and in this way obtain some measure of control over the reaction involved. Thus we may, instead of preparing free radicals by thermal decomposition, devise what is in some cases more economical, a special reaction such as is involved in the production of the $-CH_2-$ radical from diazomethane, or the methyl radical

* Paper received 25th March, 1938.

from an organic metallic compound, or the hydrogen atom photochemically by means of mercury resonance radiation.

Unfortunately there is at present no unanimity in the views held as to the mode of thermal decomposition of straight-chain hydrocarbons. Thus in the case even of the thermal decomposition of the elementary hydrocarbons methane and ethane, the following reactions have been proposed, those marked (*a*) and (*b*) being to some extent alternative views.

$$\begin{aligned} CH_4 &\longrightarrow CH_3 + H\ (a). \\ &\longrightarrow CH_2 + H_2\ (b). \\ C_2H_6 &\longrightarrow 2CH_3\ (a) \\ &\longrightarrow C_2H_5 + H\ (a). \\ &\longrightarrow C_2H_4 + H_2\ (b). \\ &\longrightarrow CH_4 + CH_2\ (b). \end{aligned}$$

Our own experiments lend support to the (*b*) rather than the (*a*) reactions, both olefines and methylene radicals being primary products of decomposition, hydrogen atoms and methyl radicals appearing only at higher temperatures. Consideration of these and similar reactions with propane and butane lead us to suppose that not only would CH_2 like CO permit us at low temperatures to build up longer hydrocarbons from shorter chains and that at higher temperatures $-CH_2-$ could be employed for breaking down straight-chain paraffins—*i.e.*, in cracking—but also that the reactions of the olefines with saturated hydrocarbons present an interesting field of inquiry.

Another method of attack is to be found in the study of the mechanism of reactions at catalytic surfaces or contact agents. The catalytic hydrogenation of unsaturated hydrocarbons dates from the fundamental investigations of Faraday and Sabatier, but the exact mechanism of the interaction of hydrogen and ethylene—for example, at the surface of nickel—is not yet clearly understood. It was hoped that when the fact was established that hydrogenating catalysts like nickel catalysed the *ortho–para* conversion of hydrogen, and when the hydrogen isotope deuterium was isolated in sufficient quantities, these new tools would permit of elucidation of the mechanism of hydrogenation. At the present moment it may be said that several new and important facts have been revealed with the aid of these reactions, but the exact mechanism of hydrogenation is not yet clear. It is found, for example, that the *ortho–para* conversion takes place readily on catalytically active metals, the energy of activation is relatively small, being some 6 kg.-cal. and the order of the reaction is less than unity. We must conclude that the conversion takes place as a result of adsorption, but direct measurement of the heat of chemi-adsorption of hydrogen on tungsten reveals the fact that the heat of adsorption is some six or seven times greater than the energy of activation for the *ortho–para* conversion. It seems difficult to avoid the conclusion that the usual concept of the mechanism of this simple reaction—viz., that it can be formulated by the reaction scheme $\underset{\uparrow\uparrow}{H_2} + \text{Metal} \rightarrow \text{Metal H} \rightarrow \underset{\uparrow\downarrow}{H_2} +$ Metal—cannot be right, and that the reaction proceeds through some sort

of exchange reaction between atoms held by chemi-adsorption and atoms in molecules held above this layer by weaker fields. This concept of exchange reactions being one of the important mechanisms in heterogeneous catalytic reactions can be revealed in another way. If ethylene and deuterium be passed over a nickel contact surface, we found that not only is dideuteroethane formed, but at the same time some of the hydrogen atoms in the ethylene exchange with those in the deuterium producing H_2 and HD in the deuterium fraction coming from the catalyst. In addition to the olefines, a number of such exchange reactions have subsequently been discovered and examined; thus Taylor found that the saturated hydrocarbons would undergo exchange with deuterium. Whilst the reaction may be formulated

$$CH_4 + D_2 \rightleftarrows CH_3D + HD$$

the kinetic mechanism cannot proceed in this way. It is found that the reaction rate is much less than the *ortho–para* deuterium reaction, consequently the rate-determining step may be either

$$MD + CH_4M = CH_3DM + MH \quad . \quad . \quad . \quad (1)$$

or

$$CH_4M \longrightarrow CH_3M + MH \quad . \quad . \quad . \quad . \quad (2)$$

followed by the rate-determining reaction

$$CH_3M + MD \longrightarrow CH_3DM + M$$

Since these reactions are taking place in the adsorbed phase, it is clear that it is impossible to decide between (1) and (2) by kinetic measurements above. The simplest method of attack is to pass mixtures of CH_4 and CD_4 over the contact agent; if the mechanism of exchange is represented by (2) we should obtain mixed methanes—*i.e.*, CH_3D, CH_2D_2, CHD_3. Experiment actually confirmed this view. In the same way the mechanism of the surface reactions involving the synthesis of ethane from methane and methane from ethane and hydrogen—

$$M{\cdot}CH_4 \longrightarrow M{\cdot}CH_3 + MH \longrightarrow C_2H_6$$
$$MC_2H_6 \longrightarrow M{\cdot}CH_3 + MH_2 \longrightarrow 2CH_4$$

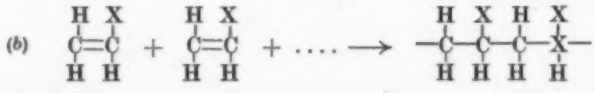
could be established. The energies of activation for the reactions on a nickel catalyst are of the order of some 14 kg. and 20 kg.-cals. respectively, the reaction taking place readily below 250° C., values to be compared with energies of activation of some 70 kg.-cals. and temperatures of some 900° C. for the more usual thermal cracking process. In this way it is possible to break and re-form C–H and C–C bonds with relatively small energies of activation, by ensuring that the radicals which are formed are never free, but always bound to the catalyst surface. Taylor's analysis of the methane ethane transformations suggests that chemi-adsorbed methyl and ethyl radicals play the rôle of intermediate compound, but it is possible that chemi-adsorbed methylene radicals may be important in some contact processes—for example, in the synthesis of olefines from water gas where cobalt with various promoters is used as a catalyst. There are some reasons for believing that the sequence of presumably reversible reactions may be written:

$$>CO \longrightarrow >C \longrightarrow >CH_2 \longrightarrow \longrightarrow [CH_2]_2.$$

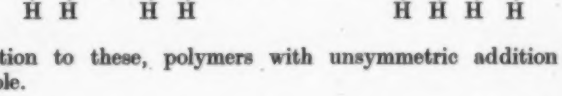
It is clearly desirable to prosecute further work into the nature of the chemi-adsorbed free radicals resulting from the act of chemi-adsorption and surface dissociation of the hydrocarbons, so as to obtain further information as to the mechanism of building up and breaking down hydrocarbon chains at catalytic surfaces. Whilst the thermodynamic data for olefine–hydrogen–paraffin equilibria are at present rather scanty, it is agreeable to note that Kistiakowsky is engaged in filling this gap. More information is at present available concerning some of the ring systems—*e.g.*, *cyclo*-hexane–hydrogen–benzene—and with an increase in knowledge of such equilibria it will be possible to take up the questions of hydrogen transfer and of selective hydrogenation and dehydrogenation in hydrocarbon systems for the production of the highly reactive polyolefines. We may also envisage the development of the use of contact agents in the fractional and selective oxidation, chlorination and sulphonation of hydrocarbons. It may be mentioned that while catalytic methods of ring formation and ring closure are by no means infrequent, no information appears available as to the possible mechanism in the opening of a ring, *e.g.* by insertion of a $-CH_2-$ radical in a six-ring which has been completely hydrogenated.

It is probable also that such studies may be important in developing methods for the polymerization of olefines in spite of the fact that with the phosphate catalyst usually employed the *modus operandi* appears to be well established as a series of chemical reactions, each involving the catalyst. We can see, for example, that a variety of polymeric chains might be formed when a mono-substituted ethylene undergoes polymerization. Thus we may obtain :—

or



In addition to these, polymers with unsymmetric addition may be obtainable.



Some of these varieties of polymeric mono-substituted ethylenes have already been prepared in the laboratory and the kinetics of their formation established. It is clear that the polymer (*b*), which is nothing more than a free radical, will grow much more rapidly than polymer (*a*), where a transfer of a hydrogen atom is involved in each link.

Colloid Chemistry Dept.,
Cambridge.

AERIAL SURVEY IN EXPLORATION WORK.*

By B. Scherpbier and J. Krebs.

Synopsis.

Aerial photography has proved to be of great value for petroleum exploration work, especially in remote countries. Photogrammetric cameras have advantages over photographic ones, also when surveying undeveloped countries, because their use entails less ground control.

By applying aerial triangulation the ground control can be reduced to the determination of ground bases 100–200 km. apart.

Aerial survey enables the exploration geologist, before entering the area to be explored, to have already available a topographical map, which very often even contains geological information derived from the photographs.

Soon after photography had been invented means were sought of applying this new technical feature to mapping. At first, attempts were made to photograph the surface of the earth by means of cameras suspended from kites and balloons. Later the aeroplane was used to bring the camera to the points from which a free and unobstructed view of the areas to be mapped could be obtained. This view was recorded by the camera, and the photograph thus obtained could be used for making a map.

The development of the aeroplane was the predominant factor in enabling areas to be photographed from the air in the systematic way necessary for aerial mapping.

During the Great War aerial photography developed very rapidly. The camera was improved, and the working of the camera was made automatic or semi-automatic. This enabled the photographer to devote his attention to other work, such as navigation.

Originally glass plates were used as a base for the sensitive layer, but soon manufacturers succeeded in making films of the size required for aerial photography.

Naturally the petroleum industry adopted this method of mapping for its exploration work as soon as it appeared that maps could thus be obtained in an economical way and at a rate unattainable by any other means.

Especially for undeveloped areas where no, or no reliable, maps exist and where petroleum exploration is to be carried out, aerial survey is of great assistance and is, in fact, practically indispensable. But it may also be extremely valuable in more developed areas, as very often the maps of these areas are incomplete and inaccurate. Moreover the aerial photographs may give valuable geological information.

Methods of Aerial Survey.

The aerial survey can be carried out :

First : as a reconnaissance. Reconnaissance flights are made over the area and photographs taken of interesting features, whilst visual recon-

* Paper received 22nd January, 1938.

naissance is also carried out. These photographs will mostly be obliques, as the area covered by an oblique photograph is larger than that shown on one taken with vertical axis. The photographs can be taken in series so that they can be connected together afterwards, but they will not cover the area completely, and only a kind of sketch map can be made from them.

Secondly: as an aerial mapping survey. In this case the whole area is systematically covered by photographs. Adequate elaboration of these enables a real map to be made. The photographs are mostly taken with the camera axis in a vertical position. Only in certain cases may the use of obliques be of advantage. They have, for instance, been applied for the aerial mapping of the Lake district in Canada, where the lakes constitute the main feature to be plotted, whilst the land is mostly flat, and moreover no detail need be mapped. We shall confine ourselves here to the vertical method of photography, as this is the more common one.

The *first* method, *reconnaissance survey*, normally is not very economical, the information obtained very often being only scanty in proportion to the cost involved. Generally it may be said that if an area is worth the money required for reconnaissance flights, the expenditure for an aerial mapping survey is also justified.

The results of reconnaissance flights might be improved by carrying out these flights at a certain fixed altitude, taking series of three photographs, one vertical, one to the left (oblique) and one to the right (oblique), the oblique pictures to be taken with the camera at a fixed angle to the vertical (about 30°) or by using multi-lens cameras.

The *second* method, *the aerial mapping survey*, will be discussed in greater detail, and will subsequently be referred to as aerial survey. The method consists in photographing the area in regular strips having a certain longitudinal overlap. The photographs of the various strips also have an overlap with regard to the adjoining strips.

Flying Equipment.

The aeroplane should be suitable for the purpose in order to make economical working possible. The ceiling, carrying capacity, speed, rate of climb, free space in the cabin, an uninterrupted view for the pilot and the navigator, a large uninterrupted angle of view from the camera hole in the bottom of the aeroplane are points which should be specially considered when deciding on a type of aeroplane.

In remote countries twin- or three-engined aeroplanes will probably be necessary to ensure safety. Freedom from vibration is also very important, as vibration leads to blurring of the photographs.

The range of the plane should be large, especially in countries where the chance of good flying weather is small, so that each spell of clear sky should be utilized to the utmost.

Crew. The photographic crew can consist of a pilot and a photographer. For mapping areas of which no reliable maps exist, a navigator may prove to be a valuable assistant, and the extra expenditure involved may soon be counterbalanced by reduction of flying time and by the better and more accurate flying of the scheme. The latter will ensure cheaper and more accurate elaboration.

The crew must be well trained, collaborate whole-heartedly and be accustomed to working in concert with one another.

Photographic Equipment.

The type of camera used is of great importance in the economy of the work.

The cameras for aerial survey may be divided into photographic cameras and photogrammetric cameras. With the first type good photographs can be obtained, but the photographs do not lend themselves as well to accurate elaboration as those obtained with photogrammetric cameras, which are, in fact, instruments of high precision with practically distortion-free lenses. In any case, the various lenses of the same type are very accurately matched. It might be said that such accuracy is normally not necessary for exploration purposes, but the photogrammetric camera is economical also for exploration mapping purposes, because when aiming at the same accuracy of the maps, the ground control can be reduced when photogrammetric cameras are used instead of photographic cameras.

The total length in kilometres to be flown to cover a certain area depends on the width of the strip covered by one row of photographs. In order to reduce the flying time, the trend has been to widen this strip, and therefore to enlarge the opening angle of the camera.

Attempts have been made to achieve this by coupling cameras together, the camera axis standing under an angle, by using multi-lens cameras, the light falling on the outer lenses being diffracted by prisms, and also by widening the opening of the single-lens camera. Until 1934 the opening angle of the single-lens photogrammetric camera was about 65°, but nowadays photogrammetric cameras are available with an opening angle of more than 90°.

Photogrammetric multi-lens cameras are available with an opening angle of 140°.

The focal length of the lenses for aerial mapping cameras varies from 5 cm. to 21 cm.

The cameras used for aerial mapping are mostly automatic or semi-automatic. They may be power-driven or hand-operated. In remote countries hand-operation might be more advisable, in view of the simpler construction.

The shutters are mostly the so-called between-lens shutters.

Focal plane shutters should not be used for aerial survey, because the picture is not exposed simultaneously.

The shutter speed mostly varies from 1/25 to 1/200 second.

On the picture appear the collimating marks by which it is possible to reconstruct the principal point, *i.e.* the point of intersection of the optical axis with the plane of the picture. Furthermore, the image of a bubble level is reproduced and a numerator is also essential. A clock might afford some advantage, and moreover the exact focal length and the number of the camera should be photographed together with the main picture. The bubble level serves to indicate whether the camera axis has been vertical during exposure. It is very important, in view of future elaboration, to know the actual position with regard to the plumb line of

the camera axis. The bubble level does not, however, indicate this accurately and reliably. Therefore another method has been developed—viz. photographing the horizon at the same time as the main photograph by means of a camera attached to the main camera. The tilt of the camera axis at the moment of exposure can be obtained by measuring the inclination of the horizon line to the line connecting the collimating marks (see Fig. 1), and by measuring the average distance between these two lines. The scale of the pictures is determined by the focal length and the altitude of the aeroplane at the moment of exposure. The focal length is known very accurately. The altitude can only be measured by the barometric method unless sufficient ground control is available on the picture from which the altitude of the aeroplane could be computed. This is normally not the case when surveying for exploration purposes.

For the geodetic elaboration it is of advantage to know the differences in altitude between the successive pictures. These can be measured by using a statoscope (a differential barometer). This instrument indicates the difference in altitude accurate to about 3 metres within a range of about 30 metres of altitude difference. It is put into operation as soon as the aeroplane is at the required altitude according to the normal altimeter. By photographing the statoscope readings at the moment of exposure of the camera, the differences in altitude are registered (Fig. 2). The absolute altitude of the pictures only affects the average scale of the pictures, and this scale can be determined later on by the geodetic elaboration based on the ground control.

We have therefore seen above that, together with the pictures of the area, photographs should be obtained of the statoscope readings and horizon photographs. The relatively small cost of the last-mentioned photographs will be more than paid for by the more rapid and accurate elaboration later on.

Photographic Material.

The photographs are mostly taken on films, as these have many advantages over glass plates—viz. less weight, no risk of breakage, easier handling, easier transport in the camera. The only disadvantage is that the film is liable to irregular shrinkage, which results in less accuracy of the elaboration than in the case of glass plates.

From the film negatives glass diapositives are very often made for the sake of safety and in order to eliminate the disadvantage of irregular shrinkage. Furthermore, for topographical and geological study paper prints are made. Printing on low shrinkage paper has advantages, because of the irregular shrinkage of the normal paper the stereoscopical image obtained will be deformed irregularly.

Flying Scheme and Ground Control.

The area to be mapped is covered by a grid of triangulation strips and by parallel so-called filling-in strips.

The triangulation strips are so projected that a grid of a favourable form is obtained, and this grid connects the available ground control.

The photographs of the triangulation strips can also be used for making

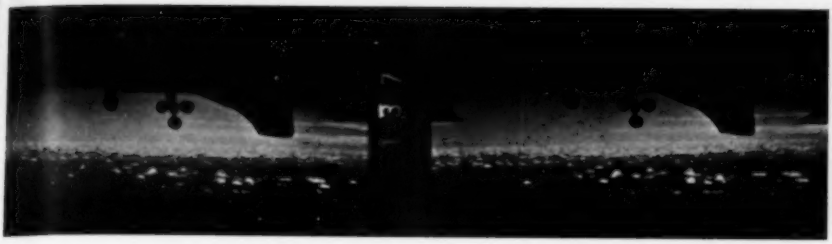


FIG. 1.
HORIZON PHOTOGRAPH.

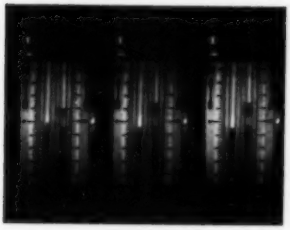


FIG. 2.
STATOSCOPE REGISTRATION.

FIG. 4.
AIR PHOTOGRAPH OF HEAVILY WOODED AREA SHOWING STRIKE DIRECTION AND MORPHOLOGICAL DIFFERENTIATION OF VARIOUS FORMATIONS.

[*To face p.* 228.

FIG. 5.

AIR PHOTOGRAPH OF HEAVILY WOODED AREA CLEARLY SHOWING FAULT AND JOINT SYSTEMS.

a mosaic, which can be used for navigation when flying the parallel filling-in strips. This is especially necessary when surveying areas of which no reliable maps exist.

It depends to a great extent on the skill of the photographic crew whether in such circumstances the flying is done according to the schemes. This is all the more difficult in areas where only short spells of good photographing weather are available, as then it often occurs that a flying strip cannot be flown entirely during one flight, so that on the next occasion the remaining part of the strip must be photographed. It requires quite a lot of navigation "sense" to be able to fly this remaining part so that there is the least possible duplication of photographs and still a good and straight strip is obtained.

The photographs are taken with a longitudinal overlap of about 60 per cent. and with a side overlap of 30 per cent. The longitudinal overlap is necessary in order to have the whole area covered by stereoscopic pairs of photographs. The side overlap is mainly necessary to avoid gaps, but it is also made use of in the elaboration.

In order to be able to locate the photographs later on, so that a map can be made, it is necessary to know the location (in a certain co-ordinate system) of a number of points of each photograph. These points could be obtained by surveying sufficient points on the ground which could be identified on the photographs. In well-developed countries sufficient points are very often available on the ground. In unexplored countries this would, however, be a costly and almost hopeless business. The necessary points can, however, also be surveyed on the photographs by a special surveying method called aerial triangulation. Instead of carrying out a field survey, the survey is carried out on the photographs in the office with the aid of special instruments.

The only terrestrial survey necessary is the determining of the co-ordinates of a few points (distanced from 100 to 200 km. apart) and base lengths in the neighbourhood of these points of a length varying between 4 and 12 km., depending on the scale of the pictures.

These co-ordinates of the ground-control points can be determined by astronomical observations if no co-ordinates are available from former terrestrial surveys.

The points and a number of points of the ground bases must be ground-marked—for instance, by white crosses of sufficient size so that they can be identified on the photographs. It is also possible to use topographical features as control points which can be identified easily and exactly on the photographs. Normally the latter method results in less accurate elaboration.

In Fig. 3 a flying scheme is illustrated on which the strips actually flown are indicated. As ground control was available from previous ground surveys, this was naturally made use of.

Elaboration.

This can be divided into geodetic elaboration and the geological–topographical elaboration.

Geodetic elaboration serves to determine the co-ordinates of the principal

FIG. 5.
AIR PHOTOGRAPH OF HEAVILY WOODED AREA CLEARLY SHOWING FAULT AND JOINT SYSTEMS.

points and auxiliary points of the photographs, so that the data obtained from the photographs can be plotted true to scale based on these co-ordinates.

It mainly consists of aerial triangulation. This triangulation can be based on the principle that the angles measured on the photographs from

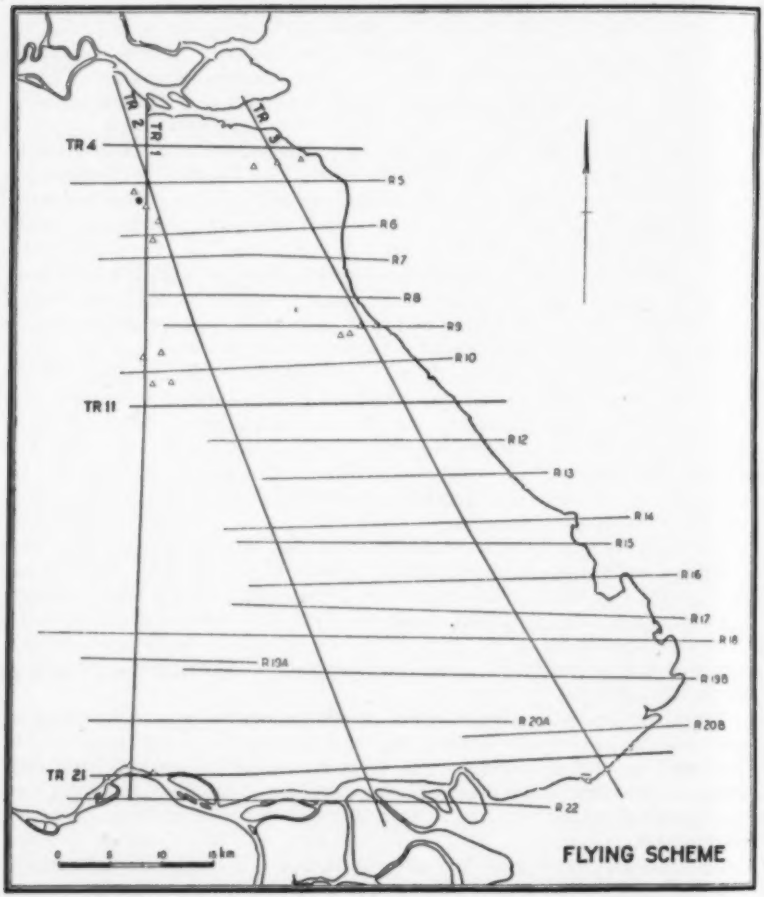


FIG. 3.

the principal point to other points on the photograph are similar to the corresponding angles in the field as measured with a theodolite. This principle is correct only when the camera axis has been vertical, errors being caused by the tilts of the camera axis, which errors are increased by differences in ground elevation, but for average tilts of the camera axis

(less than 2°) and for gently undulating country the errors are so small that the principle may still be applied.

As the principal points appear on three adjoining pictures when 60 per cent. longitudinal overlap is maintained, the angles can be measured from the principal points to auxiliary points which also appear on these photographs. By this a chain of rhomboids is obtained. When one of the sides of these rhomboids is known as to length and azimuth, the chain can be computed or plotted as a normal traverse line.

The triangulation can be carried out graphically or by the so-called slotted template method, which is an improved graphical method, or by measuring the angles with more or less complicated instruments—*e.g.* the radial triangulator—and computing the triangulation results.

When the co-ordinates of the principal points and the auxiliary points are known, the pictures can also be rectified by means of the co-ordinates of these points, assuming a flat horizontal area. The data from these rectified prints can be copied for the line map. In hilly country, and also when more accurate elaboration is required, aerial triangulation in the space will be necessary. This method exists in projecting back the details of two adjoining pictures in such a way that corresponding rays intersect. The rays may be obtained by actual optical projection or by materializing them by rods. A combination of both systems may also be used.

By this method a three-dimensional reproduction of the area photographed is obtained, from which reproduction the data can be plotted on the desired scale. This plotting is done by bringing the stereoscopic image of two measuring marks (floating marks) on the feature to be plotted. The relative movements of the floating mark against the picture-holders can be brought over on a plotting apparatus. Moreover, the above relative movements can be read off against a three-axis co-ordinate system. Normally the measuring marks and the plate-holders with the pictures are both moved.

When pictures Nos. 1 and 2 of a run have been orientated and measured, picture No. 2 is kept in position and picture No. 3 is orientated with regard to picture No. 2, and so on. In this way the data of the space-image of the whole run are obtained.

The absolute orientation of the space-image can be obtained by using the ground control.

For the main triangulation runs the more elaborate and accurate apparatus, such as the stereo-planigraph of Zeiss or the stereo-autograph of Wild, or similar instruments, should be used, whilst for the secondary triangulation strips and the filling-in strips, simpler instruments, such as the stereo-multiplex, are sufficiently accurate.

In the stereo-multiplex, instead of two pictures, up to nine or ten are orientated together. The instrument consists of a row of projectors which can be moved along rails. Each projector contains a reduced glass copy of the picture. By using red and blue filters alternatively and looking at the projection through red and blue spectacles, a stereoscopical image is obtained, and by systematic movements of the projectors the corresponding rays can be made to intersect. When this is the case, the projectors have relatively the same position as the camera at the moment of exposure. When all the projectors have been orientated in this way they can be orientated as a whole by moving the rail.

By the above method the space co-ordinates of the principal points and auxiliary points of each photograph are obtained.

The elevation is known absolutely when the elevations of the ground-control points are available, or when the surface of the sea along the coast can be used as a reference plane. For exploration maps of remote countries normally the effect of the tide in the latter case can be neglected in view of the general accuracy which can be obtained.

The above instruments can also be used for plotting details and for drawing contour lines. For exploration maps of undeveloped areas this work can be done normally by a simpler method described below. For more developed areas, when more accurate large-scale maps are desired, the above instruments can be used economically for the purpose of preparing detailed line maps and contoured maps.

For exploration maps the data can be plotted by tracing same from the prints of the photographs, using a stereoscope for better identification. The principal points and auxiliary points are plotted on sheets according to co-ordinates and on the desired scale. The above data are copied on these sheets, using the principal points and the auxiliary points as references.

Contours cannot normally be drawn accurately enough by this method, but form-lines can be plotted which will give a good impression of the general appearance of the area.

Topographical and Geological Elaboration.

From the prints all topographical data which it is possible to identify can be directly copied in the above-mentioned way. By means of a stereoscope it is possible to plot the general drainage system even in areas covered by heavy jungle.

The method is therefore most attractive for the geologist exploring more or less unknown countries. It enables him to produce a reliable topographical map right at the beginning of his exploration, a fact that contributes materially to speeding up work.

This, however, is not the only advantage the method offers, more particularly to the exploration geologist. A careful study of the photographs under the stereoscope will also reveal to him a lot of very valuable geological information. The morphology can be observed in great detail and interpreted in terms of lithology and structure. The boundary between areas of accumulation and denudation can be delineated and successive terrace levels observed. Differences of lithology can be correlated with hardness, the erosion pattern and vegetation. Faults and fold axes can often be drawn and joint directions measured. Heavy jungle does not necessarily obstruct the legibility of the geomorphological picture (see Figs. 4 and 5).

By compilation of observations on the photographs of an area which has been systematically surveyed from the air, an interpretation of the whole is obtained. This geological interpretation is of great value in directing exploration, as field parties can be sent immediately to traverse the best stratigraphic sections and to examine likely structures.

AN OPEN-HOLE CEMENTATION.*

By Wm. Darling and G. Cotton, B.Sc., F.G.S. (Associate Member).

The following is a description of what the authors believe is an unusual method of shutting off water in drilling for oil, although a somewhat similar process is used in mining practice when sinking shafts.

The test well at Edale in North Derbyshire had been drilled to a depth of 422 ft., and from 346 ft. to 419 ft. a succession of limestone beds with intercalated shales had been penetrated: these limestones carried a considerable volume of water (in excess of 300 barrels per day), but the head was comparatively low, the standing water level being 200 ft. from the derrick floor. Continuous bailing failed to lower the water more than 100 ft., and as this water might mask any oil shows struck below, it was deemed advisable to shut this water off. As there was no means of knowing whether or not other water-bearing strata would be encountered below, the Company did not wish to reduce the size of the hole by cementing a string of casing.

The limestone penetrated appeared in core samples to be hard and impervious, and it was therefore thought that the water was coming from fissures in the limestone rather than through the limestone itself: this view was confirmed by the large volume of the water under comparatively low head.

It was found that the hole could be filled with water, but that the level thereafter fell at the rate of 8 ft. per minute until it again reached its standing level. The cementation was carried out in the following manner:—

The hole was filled with water and kept full while cement was being mixed. Five tons of cement were mixed in a trough on the derrick floor, the mixture being estimated to consist of 42–45 lb. of water per 100 lb. of cement, and the mixed cement was poured down the well, water pumping being stopped at this time. After all the cement had been poured in, sufficient water to fill 100 ft. of the hole was pumped in on top. The level of the top of this water was watched by means of a float on a measuring line; the level fell to 170 ft., and as it was then falling very slowly, two lots of water, each equivalent to 25 ft. in the hole, were put in, and, as these had little effect, the hole was then filled with water. The level fell very slowly for a few hours, and then remained practically stationary.

After a shut down for 5 days for the cement to set, the top of the cement was found at 326 ft., or about 20 ft. above the top limestone bed. The cement was drilled out and the hole was found to be perfectly dry. It is estimated that about 3 tons of the cement were displaced into the cracks in the limestone.

The conditions for this type of cementation were excellent, in that the cement could be forced into the fissures with only the pressure of the head of water above it, and it is realized that the method is applicable only in such circumstances.

In conclusion, the authors desire to thank Messrs. Steel Brothers & Company, Ltd., for permission to publish the above.

* Paper received 5th February, 1938.

DISCUSSION ON DEWAXING.

Reply from Dr. BRUNO ENGEL.

*Reply to Mr. F. E. A. Thompson.**

A PHASE separation sometimes takes place also when dewaxing with heavy solvents and combinations thereof. By varying the solvent composition, however, such separation can be prevented, as is the case with the frequently modified so-called acetone-benzol process. In the case of a phase separation, oils with low viscosity index and viscous solidification are obtained, particularly from mixed-base products, whereas if no phase separation occurs, oils with high V.I. and paraffinic solidification are obtained. A *direct* comparison between such dewaxed oils obtained from a certain stock with and without phase separation, respectively, would be entirely misleading, unless the viscous-solidifying oil is refined prior to the pour-point determination, whereby the refining losses must be taken into consideration when calculating the yield. In order to avoid misunderstandings and erroneous conclusions, only such examples have been mentioned in the author's paper which refer to treatment without any noteworthy phase separation. Consequently only such pour points and corresponding yields have been given which can be directly compared.

Reply to Messrs. V. A. Kalichevsky and R. Lee.†

For a fresh paraffinic distillate or raffinate an addition of only 0·1 per cent. or less of an inhibitor (synthetic oil, pour-point reducer) is sufficient to effect a certain increase of the yield of dewaxed oil in the presence of chlorinated hydrocarbons. When treating residues or aged or mixed-base products, on the other hand, it is often necessary to add not less than 0·5 per cent. or more of the inhibitor to obtain a corresponding effect. This proves that certain polymers or isoproducts more or less eliminate the favourable effect of the inhibitor.

If the dewaxing is not carried out with chlorinated hydrocarbons as a solvent, but instead with *e.g.* gasoline (naphtha), the difference between the minimum quantities of the inhibitor to be added is considerably greater. When treating fresh and paraffinic distillates, the minimum quantity is about 0·15 per cent., viz. about the same as when using chlorinated hydrocarbons. With a mixed-base product, on the other hand, or a product rich in polymers, for which only 0·5 per cent. inhibitor is required when using chlorinated hydrocarbons, the quantity has to be increased to 5 per cent. and more, in order to obtain a measurable effect on the yield when dewaxing in naphtha dilution. In many cases the presence of naphtha entirely eliminates the effect of the inhibitor. This indicates that the colloidal nature of certain high-molecular oil components,

* See *J. Instn Petrol. Tech.*, 1937, **23** (170), 757.
† See *ibid.*, 1938, **24** (171), 60–62.

adsorption phenomena, etc., which occur particularly when dewaxing with propane, naphtha, etc., play a partly unknown rôle in connection with the inhibitor effect.

The examples quoted in the article refer, however, to tests which were first carried out on a laboratory scale by the aid of suction filters, and later on with discontinuously working centrifuges. Only then was the application on *continuously* working centrifuges (type Separator-Nobel) made, on which that information was based to which Messrs. Kalichevsky and Lee refer in their question.

ERRATUM.

In the December 1937 number of the *Journal* on page 745, U.S.P. 1,815,022 cited in the literature, was assigned to the Standard Oil Company of Indiana. This should have been the Standard Oil Development Company.

OBITUARY.

JOHN MALCOLM MUIR.

Mr. John Malcolm Muir, a member of the Institution since 1920, died in Sydney, N.S.W., Australia, on January 19th, 1938, in his fifty-third year.

John Muir was born at Uddingston, Scotland, and was educated at Glasgow and Edinburgh. After four years on H.M. Geological Survey, principally in Wales, he went to Mexico in 1912 in the days of the early development of the Panuco Field, and was the recognized authority on sub-surface correlation in that region until his departure in 1935.

He then joined the staff of the Turkish Petroleum Company, and from 1927 to 1937 was engaged in petroleum geology and geophysical interpretation in the United States and Mexico.

At the time of his death he was chief geologist of the Island Exploration Company, Ltd., his field headquarters during the past year having been at Daru, Papua.

In 1936, the American Association of Petroleum Geologists, of which he had been an active member since 1924, published his memoir, entitled "Geology of the Tampico Region, Mexico," which is indispensable to the appreciation of the stratigraphy and occurrence of those great oil deposits. In this book acknowledgments to other students abound, thereby reflecting the modesty of the author, but justice requires that his own prodigious industry and critical powers of observation be acknowledged here, as it is already known to everyone who has worked in the Mexican Fields.

P. W.

A. E. DUNSTAN, D.Sc.
REDWOOD MEDALLIST, 1938.

[*Frontispiece.*

UNIV. OF MICH.

REDWOOD MEDAL.

Dr. A. E. Dunstan.

The Council of the Institution of Petroleum Technologists has awarded the Redwood Medal of the Institution to Dr. A. E. Dunstan in recognition of his distinguished services to the science and technology of petroleum.

The conditions of award of the Redwood Medal are that it shall be awarded "not more than once in each year, to a petroleum technologist of outstanding eminence, irrespective of nationality or membership of the Institution." Under these conditions the Redwood Medal has been awarded on three occasions—viz., 1932, Dr. L. Edeleanu; 1934, Dr. David White; 1936, Mr. Harry Ricardo.

Dr. A. E. Dunstan was born at Sheffield in 1878. He was a Foundation Scholar of the Royal Grammar School, Sheffield, and a Scholar of University College, Sheffield. In 1899 he entered the Royal College of Science, South Kensington. Later on he studied at University College, London under Ramsay and at East London College under Hewitt.

At University College Dr. Dunstan worked with Trouton on investigations into the correlation of physical properties and chemical constitution. He had already published work on viscosity-concentration curves of mixtures. This work was continued at University College and elsewhere, and formed the subject of his thesis in 1910 for the degree of D.Sc. In the meantime he had communicated numerous papers to the Chemical Society on the problems of viscosity in collaboration with Thole, Wilson, Hunt, Stubbs and others. He was elected a Fellow of the Institute of Chemistry in 1918.

From 1905 to 1915 Dr. Dunstan was head of the Chemical Department, East Ham Technical College. In 1915 he joined the Anglo-Persian Oil Company. In the same year he was elected a Member of the Institution of Petroleum Technologists. From that time dates the important series of researches on the chemistry and refining of petroleum with which Dr. Dunstan's name is particularly associated. The first important paper relating specifically to the petroleum industry was presented to the Institution in 1916 by Dunstan, Lomax and Thole, and dealt with the Pyrogenesis of Hydrocarbons. It described the evolution of the process of cracking and of the principles underlying it. Dunstan and his collaborators were at that time engaged in the manufacture of toluene on a large scale for purposes of national defence.

A period of intensive research followed on the chemistry of refining processes, during which experimental work was carried out at Abadan and Sunbury. At that time the refining of petroleum fractions was chiefly achieved by sulphuric-acid treatment. Dunstan and his co-workers were

able to show that the deleterious components of straight gasoline were ordinary organic derivatives of sulphur, and could be removed by treatment with alkaline hypochlorites. Looking back, it is easy to realize now the simplicity of the oxidation processes concerned, but in 1917 desulphurization was still in the empirical stage. The key to successful commercial desulphurization by hypochlorites was discovered by Dunstan to be the quantity of free alkali present—a quantity which could only be allowed to vary within narrow limits. An account of Dunstan's early work on hypochlorite treatment was published in the *Journal* in 1924.

Following his work on hypochlorite treatment, Dunstan, in collaboration with Thole, investigated solvent refining methods, and in particular the liquid SO_2 treatment associated with the name of Edeleanu. This process, described in the first instance by Edeleanu in 1907, had been proposed by Dunstan during the War as a means of obtaining toluol from petroleum distillates. Its extension to the refining of light distillates was the subject of researches carried out between 1920 and 1923.

Thereafter followed a series of investigations into the nature of the components of lubricating oils, the identification of the constituents which provide an unbroken and unbreakable film, and the correlation of these with the nature of the surface on which they act. This is a field of research which is still widely engaging the attention of physicists and chemists.

Altogether Dr. Dunstan has contributed over 100 papers to scientific societies and periodicals either alone or in collaboration with others.

In 1928 he delivered the Cantor Lectures to the Royal Society of Arts.

Dr. Dunstan is Chief Chemist of the Anglo-Iranian Oil Company and a Director of National Oil Refineries, Ltd. He was President of the Institution of Petroleum Technologists from 1929 to 1931, and has been a Member of Council since 1919. He has been Honorary Editor of the Institution's publications since 1920.

He is Honorary Chairman of the Committee on Petroleum Products of the American Society for Testing Materials; former member of H.M. Fuel Research Board; a delegate of H.M. Government to the 2nd World Petroleum Congress; Chairman, Petroleum Committee of the Imperial Institute Mineral Resources Division; Member of the General Council of the British Standards Institution; former Vice-President of the Institute of Chemistry and of the Society of Chemical Industry; and Member of the Royal Institution.

The achievements of Dr. Dunstan in an editorial capacity are scarcely less distinguished than his contributions to science. It is largely due to his constructive and critical judgment that the *Journal of the Institution of Petroleum Technologists* has attained its high international reputation. The *Journal* has been the medium for the publication of several hundreds of papers of the highest calibre. It has grown from a small quarterly to an established monthly periodical, with an authoritative Abstracts Section, almost as large as the "Proceedings" Section. It is very largely due to the ideals and leadership of Dr. Dunstan in attracting enthusiastic co-workers, that these developments have been possible.

Other publications of the Institution which have appeared under the General Editorship of Dr. Dunstan include the "Crystal Palace Lectures

on Petroleum" (1924), "Proceedings of the First World Petroleum Congress," 2 vols. (1934), "Twenty-five Years' Retrospect" (1935), and the "Annual Reviews of Petroleum Technology" (1936 and 1937). Finally, as Managing Editor of the recently published "Science of Petroleum," Dr. Dunstan and his co-Editors have produced a work which, both in conception and execution, will stand unrivalled for many years to come.

THE REDWOOD MEDAL

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

AWARD OF REDWOOD MEDAL AND PRESIDENTIAL ADDRESS.

THE One Hundred and Eightieth Meeting of the Institution of Petroleum Technologists was held at the Royal Society of Arts, John Street, Adelphi, W.C., on Tuesday, 12th April, 1938, at 5.30 p.m., Lieut.-Col. S. J. M. AULD, O.B.E., M.C., D.Sc., President, in the Chair.

THE REDWOOD MEDAL.

The PRESIDENT announced that the Council had awarded the Redwood Medal of the Institution to Dr. A. E. Dunstan in recognition of his distinguished services to the science and technology of petroleum.

The PRESIDENT said that for Dr. Dunstan to receive the Medal, which was the most signal honour that the Institution of Petroleum Technologists could bestow, was a source of great personal gratification to Dr. Dunstan's many friends, of whom he was glad to count himself amongst the oldest.

The Institution was proud to think that with the whole world to choose from there should be no question of Dr. Dunstan's pre-eminence and his outstanding worthiness of the award. Dr. Dunstan had many great qualities, but he thought the greatest of them all was the fact that throughout all the years he had never lost his sense of vision.

Special messages of regret for their inability to be present had been received from Mr. Alexander Duckham, the donor of the Medal, and from Mr. Eastlake, the Hon. Secretary, with whom Dr. Dunstan had been associated for so many years. They regretted very much that they were not able to be present and to join in the congratulations which members now extended to Dr. Dunstan.

The President then presented the Medal to Dr. Dunstan, wishing him health and opportunity to continue his fine work on a subject upon which he had already left so clear a mark.

Dr. A. E. DUNSTAN, D.Sc., F.I.C., said it gave him the utmost pleasure to receive the Medal at the President's hands. He did not know how many years it was since the President and he had studied at the same college and under the direction of that eminent chemist, Professor Hewitt. Later on they had been colleagues in the same company, and for over thirty years he had been proud to reckon himself as one of the President's personal friends. For the award itself he wished to express his deep gratitude to the Council, to whom he was not entirely unknown, for he

had worked with them and many other Councils before them. He could truly say that his work with the Council of the Institution of Petroleum Technologists had been to him a veritable joy. He could say precisely the same about his fellow-members of the Institution. In that connection he could not avoid quoting a saying which he frequently repeated, a saying of Plato: "The aim of a veritable community is not that this man or that man should prosper, but that all should flourish." What a motto was this for the Institution of Petroleum Technologists to adopt!

The award of the Medal, which was the highest honour the Institution gave to its members or to anyone outside its list of members, inevitably brought back reminiscences. He could remember Mr. Alexander Duckham, who had been associated with Sir Boverton Redwood for many years and wishing to honour Sir Boverton's memory, had provided the Medal. He thanked Mr. Duckham, and he could not help thinking of Sir Boverton himself—that great figure in the history of petroleum technology, that immaculate and meticulous gentleman with an extraordinary command of English and an encyclopædic knowledge of the whole science of petroleum, who had adorned every subject he had discussed and had conferred lasting lustre upon the Institution. It was Sir Boverton who had brought him into the orbit of the Institution, and it was he who had ultimately put him in charge of the *Journal*. He could remember also the next President, his own chief, Lord Cadman, who had done yeoman service for the Institution, and who in fact was alone in having served the Institution twice as President and who was to-day an outstanding figure in the industry, and to whom also the Institution was very dear. He could see in imagination a galaxy of talent, a series of most able men, Past Presidents all—Lord Greenway, Sir Frederick Black, Sir Thomas Holland, Herbert Barringer, Professor Brame, Mr. Adams, Mr. Dewhurst, Mr. Kewley, and not least Col. Auld; also Mr. Eastlake—who had served the Institution so well and so honourably and so intensively for long years. It had been to him an immense happiness to have the privilege of serving the Institution with these great men.

His own particular activity had been in the *Journal*. His first Editor had been the late W. H. Dalton, incomparable in his English, indefatigable in his work. Eighteen years ago his mantle had fallen on himself. The *Journal* had naturally and reasonably grown with the Institution. It was the Institution's *Journal*; it reflected its growth and its importance; and he wished on that occasion to give thanks to the many ardent workers with whom he had been associated during those eighteen years. He wished specially to mention Mr. Sell, who had helped him for so many years, Dr. Garner, the Secretary, and the new Assistant Secretary, Miss Tripp. All these had done the most admirable service, and he did not propose to stand there and take the credit for it without that acknowledgment to his colleagues, the abstractors and the contributors. Finally, he wished to pay tribute not only to all his friendly collaborators, but also and especially to Lord Cadman under whom he had served for so many years.

In conclusion, Dr. Dunstan said that the Institution was to him so much more than a mere formal society. To him it was a very real and live association of live members. It was now to be reincarnated into a more

important body, with more widespread activities and facilities, with active branches throughout the world. It was the responsibility of all members to see that it went on from strength to strength.

Professor BRAME said it was his privilege as the senior Past-President at the meeting, and his pleasure as an individual, to ask members to accord a most hearty vote of thanks to the President for the very able and stimulating address which he had given that evening. The meeting did not, of course, discuss Presidential Addresses, but he might be permitted to go so far as to say that it had been a very valuable piece of work to give the résumé which the President had given of the past activities of the Institution, to hold up the mirror, as it were, before members so that they might possibly admire themselves a little; but he certainly thought that it was a most wise choice of subject at that juncture in the affairs of the Institution.

The vote of thanks was carried with acclamation.

The PRESIDENT formally replied, and the meeting terminated.

PRESIDENTIAL ADDRESS.

THE INSTITUTION AND THE INDUSTRY.

By Lt.-Colonel S. J. M. Auld, O.B.E., M.C., D.Sc.

In the course of events there come times when it is desirable to halt for a moment and take stock. In the history of the Institution of Petroleum Technologists this, I think, is such an occasion. It is not my wish to use this opportunity for the mere purpose of summarizing the past. It is rather to see how far we have fulfilled our obligations to that past and where we stand in relationship to our covenant with the future.

My address is likely to be the last given by a President of the Institution of Petroleum Technologists. Important changes in the name and in the constitution have been decided upon by the members, and now only await the formal ratification of the appropriate Government department. It is fitting, therefore, that we should give thought to the intentions of the founders of the Institution, to what has been accomplished during the twenty-four years of its being and to what we, as the torch-bearers, intend to prepare for the years to come.

The quarter of a century which has lapsed since the Institution of Petroleum Technologists was incorporated under licence from the Board of Trade has depleted the ranks of the founder members. We are fortunate, however, in having with us in most active co-operation some half-dozen of the original officers, including one of the two first vice-presidents. This continuity is of even greater importance to us than the big part which these members continue to play in the administration. It ensures a succession of effort and of purpose which, for collective bodies, as for individuals, is the criterion of ordered thought and deed. It is natural that we should seek amongst the sayings and actions of these men some clue, some expression, indicative of their early thoughts; of their intimate identification with the activities of the Institution; and their views as to its future. This clue is not far to seek. It can, I am convinced, be expressed in one word—*education*. The education of oneself, of one's fellows, one's pupils, not infrequently of one's masters; of the industry as a whole, of the community at large. This is a concise picture of the broadening of the basis of our knowledge and the complex organization that has been elaborated for its dissemination. This we have come to regard as the Institution itself, and this indeed the Institution really is.

In his inaugural Presidential Address our Founder President stated the aims of the Institution to be firstly,

> "To enable technologists engaged in the petroleum industry or shale oil industry to meet and to correspond, and to accumulate trustworthy information . . ."

and secondly,

> "To promote the better education of persons desirous of becoming professional consulting petroleum technologists, petroleum engineers, geologists or chemists, and to elevate the professional status of those employed in the petroleum industry. . . ."

In those days the consulting professional technologists loomed largely on the petroleum horizon. With the exception of Government officials, indeed, they practically dominated the technical side of the oil industry. It is more than significant, therefore, that both as regards the accumulation and exchange of knowledge relating to, and on behalf of, the industry, and as regards the elevation of the professional status of those employed in it, these very men—leaders in the foundation of the Institution—should have formulated their aims by phrase and by implication upon recognition of the need for education.

Things have changed very much in the composition of the membership of the Institution since then. There followed hard upon the heels of the Consultants a whole army of professional men who were the servants and associates of the individual oil companies and corporations. They brought with them a new outlook, new knowledge, team work and an almost fanatical zeal for investigation. Their numbers swelled the ranks of the Institution and their work its *Journal*. Moreover, they carried the interest of their administrative colleagues, and thus fulfilled the hope expressed in the first editorial of the *Journal* to the effect that

> "the Institution is worthy of the most cordial support of all those who are interested professionally or commercially in the petroleum and shale-oil industries."

The support from the industry was practical. Financial assistance was forthcoming to enable permanent officials to be appointed, and thus relieve the honorary officers of much of the tremendous amount of work which was accumulating. Special individuals were accorded time to enable them to undertake organizing and editorial duties. Employees were encouraged to attend meetings and to write papers. Help was given in the matter of premises. All of these things have waxed rather than waned with the passing of time. So much so that it is difficult to be too appreciative of what the industry has done for the Institution. Unworthy voices have suggested that it may have done over-much; that by its assistance the industry may have disbenefited the Institution and lowered its independent status. Nothing could be farther from the truth. The liberty of action of the Institution has been safeguarded by a whole succession of wise councillors. Its inviolability and its freedom from dictation from outside are amongst its proudest tenets. Moreover, in reality the balance due to gratitude is preponderatingly on the other side. What the industry has done for the Institution is small in comparison with what the Institution has done for the industry, and what in its new form it will continue to do. On this matter I feel deeply.

Early in its history Lord Greenway spoke of what the Institution of Petroleum Technologists had done in centralizing attention upon the

industry. That is still true to-day. What is still more to the point, however, is that it has made the industry look at itself. It has consistently held up for inspection the progress made elsewhere. It has directed attention to the potentialities of those basic discoveries of to-day which may become the leading industrial practice of to-morrow. It has influenced the discard of empiricism and the general adoption of standards. It has acted as a recruiting-ground, both for thought and personnel, by attracting to its deliberations the best intellect in this country and abroad. It has encouraged the University education of its neophytes and the use of the University staffs as advisers. It has developed an internationalization of thought and association which has acted as a beacon to encourage the formation of similar societies in other lands. It has kept itself in the forefront of all these and many other activities for the abiding benefit and to the enhancement of the reputation of the petroleum industry.

These are things that cannot be bought with money. They are vital. They represent the devotion of the councillors of the Institution, and their unflagging zeal in committee. They are indicative of extensive and onerous work accomplished by the executive officers—often by the light of the midnight oil and at the expense of personal relaxation. As much as anything, however, they portray the loyalty and solidarity of the ordinary members of the Institution, without whose support nothing could be done. It is often, indeed, the rank and file who have supplied the impetus to the various activities upon which the Institution has embarked.

Such things are all measures of enthusiasm and aliveness. They indicate. more clearly than my insufficient words can say, how much the Institution has been the spiritual home of the industry and how worthily it has fulfilled that function.

As I have already indicated, I feel that the great word "Education," as used in the relationship of the Institution to the industry, should be applied only in second place to the scholastic instruction of its individual members. Much has been done in that direction by fostering the scientific training of the young men about to enter the industry, and successive Presidents have reviewed the methods adopted and the success attained. Whatever help could be given, collectively, or by encouragement of the participation of individual members, has, of course, been accorded fully and willingly. Scholarships have been founded, prizes offered and special lectures provided. It has been fully realized that the strength of the Institution would be determined by its ability to attract the right sort of men to the industry, and at the same time to raise the standard of knowledge of those already within it. In consequence the relationships with the University of Birmingham's department of Oil Engineering and Refining and with the Department of Oil Technology of the Imperial College of Science and Technology have been of the closest. Of scarcely inferior importance has been the less official intimacy with the Sir John Cass Technical Institute, which in London has done so much by means of its courses and lectures to inspire and to fulfil the desire for technical knowledge amongst those members of the oil industry to whom training in petroleum technology would otherwise be denied. At the same time, the Institution has given considerable thought to the strengthening of the Students Section, a subject in which I am greatly interested and on behalf

of which I grasp this opportunity of appealing once again for the maximum support from all senior members.

The real education of the industry, to which I refer, is not of this directly instructional kind. It is provided rather by the Institution and its individual members in the form (*a*) of making readily available organized modern knowledge; (*b*) taking steps for the establishment of increasingly higher standards of work.

You will notice how closely these parallel the intentions of the founders as expressed by the Founder President. The chief divergence is in (*b*), for the second principal objective of the Institution would not now appear to be the professional education of consultants and the personal standard of attainment of the members so much as the raising of the tone of the industry as a whole. How successful this has been I have remarked upon elsewhere, for even in an age of industrial achievement the economic and technical efficiency of the petroleum industry is outstanding.

Let us first consider the making available of knowledge.

The "Journal."

Without the *Journal* it is not conceivable that the Institution could exist. With a less potent journal its activities would have been stultified and its survival possibly jeopardized. To-day the *Journal of the Institution of Petroleum Technologists* is recognized throughout the world as one of the most authoritative sources of information concerning petroleum. It is read in every oil-producing country, and probably in every oil-using country. It is scarcely too much to claim that it has the highest reputation of any scientific journal or periodical devoted solely to the study of petroleum. This enviable position has been reached partly by virtue of the careful choice of the communications and papers which are published, and partly because of the high standard of the grouped Abstracts. Developed from a small beginning, the Abstracts soon replaced the "Current Bibliography" which had been an earlier feature of the *Journal*. Last year over fifteen hundred separate papers were abstracted, amounting to nearly five hundred close-type pages of the *Journal*. The value of these Abstracts is considerable. Their group classification has made them almost unique. It is small wonder that they are regarded, as I can assure you they are, by people in many countries as the starting-point for the collation of information preparatory to engaging in an investigation, or as a means of keeping abreast of the times.

Second only to the Abstracts in this respect are the Annual Reports on the Progress of Naphthology. These were started in 1924, and are amazingly fine summaries of what has happened in petroleum technology in each year preceding publication. The Reports are now issued separately from the *Journal* proper, and are in great demand. The individual contributors to these synopses are chosen with considerable foresight. They are all specialists in the subjects on which they write, and it is possible thereby to introduce even into such compressed summaries an appreciable amount of critical thought and helpful deduction.

It is still, however, as the record of the transactions of the Institution that the *Journal* mirrors the individual activities of its members, and

thereby most directly influences thought within the industry. It is significant, therefore, that although the format of the *Journal* has had to be enlarged, its page-bulk continues to increase. Of still greater significance is the undoubted fact that the average standard of the communications becomes progressively higher. This is particularly marked as regards the uses of petroleum products. To mention only one subject, I would suggest that the various papers relating to combustion within the internal-combustion engine which have been read during the last few years before the Institution have been of outstanding excellence, and have had great influence both on the trend of development within the petroleum industry and on engine design.

The catholicity of the subjects dealt with is also noteworthy. It is interesting in that respect to compare the present *Journal* with that of a number of years back. Proportionately the space given to the application of petroleum products is much greater. That may perhaps be in the way of more nearly striking a correct balance. In the earlier days, when exploitation was of the greatest importance, territorial descriptions quite rightly required outstanding prominence. With the tendency of the industry to swing from an analytical towards a synthetic type of operation, the present more comprehensive outlook was to be expected.

A further advance in the presentation of papers and addresses has been made of recent years by holding General Discussions on subjects of interest. When several papers are offered dealing with different aspects of the same matter, it is possible, with advantage, to promote joint discussion and to arrange for simultaneous publication. In many cases a complete number of the *Journal* has been reserved in this way for one subject, to the great benefit of the specialists interested and the encouragement towards bringing themselves up-to-date of the remainder.

Individuals gain their most intrinsic education by mixing with others and learning not only from their own, but from other people's experience. Man does not live to himself alone, and it is doubtful whether an institution can live to itself alone. In any case, it is certain that no industry lives only to itself. So much is gained by association that it has become the custom in recent years for learned and professional bodies to organize joint meetings for the purpose of airing and discussing subjects of common interest and joint importance. In this respect the Institution has been zealous. A large number of joint meetings have been organized by ourselves or participated in with other societies.

Discussion on Lubrication and Lubricants.

By reason of its scope and significance, I venture to mention the General Discussion on Lubrication and Lubricants held last year under the ægis of the Institution of Mechanical Engineers. The part played by the Institution of Petroleum Technologists on the occasion of that three-day meeting was large. By virtue of a particular interest in lubricants and lubrication, it was natural that the Institution should bring much to the Discussion. It is certain that both individually and as a whole it brought still more away. Spencer was insistent that this form of education is the most vital known to man. We need not question that in the sequence of

transference of knowledge readiness to learn and willingness to impart are of equal and transcendent value. I should like to claim on behalf of the Institution that it has never failed in either of these respects; that it works with waxing enthusiasm for the advancement of knowledge, and that its reward is in seeing the growth to maturity and being in commutual relationship with an established, well-ordered and well-guided industry.

Chemical Standardization.

Education through precept is notably surpassed by education through example. Example is active; it is constructive; and it is well and truly paraphrased as standardization. Standardization in its turn has been, in fact, one of the most effective activities of the Institution of Petroleum Technologists. I should like to say a few words on the one side concerning the Standard Methods for testing petroleum and petroleum products, and on the other concerning the work on engineering standardization which has occupied some of our attention during recent years.

It was in 1917 that Mr. Alexander Duckham wrote to the Institution, on the occasion of the presentation of a paper by Mr. E. Lawson Lomax on the Testing and Standardization of Motor Fuel, suggesting that there should be appointed a Standardization Committee whose reference should be to investigate methods of testing and to recommend standards for adoption in this country. That is quite explicit. Directly on that foundation was built the elaborate and commanding structure of the Chemical Standardization Committee, whose work commands so much respect and has reflected the greatest credit upon the Institution as a whole.

The Committee was ultimately formed in 1921. I presume the war was responsible for the delayed action. Since then, however, its work has been practically continuous. Late in 1922 Dr. Dunstan read a paper before the Institution summarizing the work which had been carried on to date, and dealing in particular with the deliberations of the various sub-committees which had been formed to deal with special problems.

At that time there were seven members of the Standardization Committee and twenty-three co-opted members, sitting under the Chairmanship, very rightly, of Mr. Duckham. The Committee operated through six sub-committees. The subjects concerned were Naturally Occurring Bituminous Substances; Distillates up to Kerosene; Kerosene and Intermediates; Lubricants; Liquid Fuels; and Asphaltum and Artificial Residues. The book "Standard Methods for Testing Petroleum and its Products" was first issued in 1924. A second edition was published in 1929, and a third in 1935.

It is interesting to see how things have developed since then. By the time the 1935 edition of "Standard Methods" appeared the Committee had grown to thirteen members and eighty-one co-opted members. It now operated through ten sub-committees and ten panels. The original sub-committees had been split up and extended. Subjects of the importance and modernity of Knock Rating had appeared, and Kerosine was now spelled with an "i."

The panels dealt with the following matters: Gum in Gasoline; The Tendency to Smoke of Kerosine; Viscosity; Lubricating Greases; Turbine

Oil; Spontaneous Ignition Temperature of Fuel Oil; Cut Backs and Fluxes; Wax in Bitumen; Tar-Bitumen mixtures and Knock Rating of Motor and Aviation Fuels.

In addition, part of the work of Sub-Committee No. 10 had been published separately in 1932, under the title of "Measurement of Oil in Bulk: Part I —Standard Weights and Measures."

Everybody having to deal with the testing of oil knows the "Standard Methods." To many chemists outside our own industry they *are* the Institution of Petroleum Technologists. They are embodied in many British Standard Specifications; they are used by Government Departments; they are frequently referred to by local authorities and other professional associations; more and more they are being accepted as the sole reference for the testing of petroleum by commercial bodies of the most diverse interests. Internationally they are recognized by other standardizing bodies. In this respect I would refer particularly to the close collaboration of the Chemical Standardization Committee of the Institution with Committee D-2 of the American Society for Testing Materials. A number of the A.S.T.M. methods have been adopted. In the case of new and tentative procedure, interchange of experience and of data between the two bodies permits development along identical or closely similar lines, and is probably the most practical form of international standardization existing.

In the Preface to the latest edition of the "Standard Methods," the Chairman of the Chemical Standardization Committee writes, "Not only the Institution, but the industry as a whole and the users of petroleum products are indebted to the members of the Chemical Standardization Committee who have so willingly given a great amount of time to the work."

I should be sadly lacking in the courtesies of acknowledgment if I did not grasp the opportunity which my position offers to point out that these achievements are largely due to the leadership and devotion of the Chairman of the Committee who penned those modest words—Professor J. S. S. Brame.

Professor Brame has been a member of the Committee since its formation, and its Chairman since 1928. That to many people would be long enough to get wearied of well-doing. With him it seems to create fresh enthusiasm and a determination to reach out into new realms of usefulness.

I wonder, however, whether even Professor Brame and his helpers realize the full value of the job to which they have so freely turned their hands.

Their work is not merely the preparation by a number of chemists and their collaborators of a series of standards for the benefit of those interested in the testing of petroleum products. However creditable that may be to the Institution and to the individuals concerned, it does not measure the effect which the standards have had upon the industry. Motion we know to be relative, and without a yard-stick of some kind it is not possible to measure progress. What psychologically is of considerable moment is that the establishment of yard-stick records is in itself a great incentive towards their improvement. The fact that a scoring-board exists is sufficient in itself to account for high scores. This stimulus need not be ascribed

merely to the desire to notch centuries or to break a record. It is the expression of man's continuous effort to work towards an ideal. Set up a standard of any kind, and its attainment, or its preservation, will become the preoccupation of its devotees. This, I should like to think, is the inner meaning of our own Standards. They inculcate the worship of an ideal not only by encouraging the more and more exact measurement of the individual properties with which they are concerned. They constantly stimulate the production of materials which can be and are worthy of being so measured. I have heard it stated that a chemist is a man who goes to infinite pains to produce pure materials on which he is content to make the most inexact measurements; but even a chemist will not weigh to milligrams on a balance which is only accurate to a gram. Give him accurate tools, call for exact data, turn him so to speak into a physicist, and his products become more and more worthy of the demanded precision. What is more, he will quite likely bring forward fresh materials of different nature and produced from an almost sub-conscious desire to go one better.

We cannot fail to trace these things in the actualities of the petroleum industry; and I commend the thought to you that the Standardization Committee of the Institution has done much to raise the whole technical level of the industry, and not merely the tone of its testing Laboratories.

Engineering Standardization.

There is another aspect of the Institution's standardization work of which I would make mention. It concerns a subject of which little is known to the ordinary members of the Institution. I refer to the Engineering Standardization Committee, which was appointed by the Council in 1932.

The duties of this Committee are: (*a*) To Act as advisers on Engineering matters to the Chemical Standardization Committee, and (*b*) To consider the production of Engineering Standards for the Petroleum Industry and to make recommendation to Council (1) in conjunction with the British Standards Institution, and (2) on their own initiative.

For very plain reasons the Engineering Committee works along different lines from the Chemical Committee. The petroleum industry as a whole works to such an extent on A.P.I. specifications for equipment that in the majority of cases it is undesirable for separate British specifications to be set up. In the second place, the responsibility for the issue of British Engineering Standards is that of the British Standards Institution. Where such standards are required or should be issued on behalf of the petroleum industry, it is obviously desirable that they should be issued by the B.S.I.

This latter important point was agreed upon at joint meetings with the British Standards Institution. It was further agreed that the B.S.I. should appoint representatives from the Institution on its principal engineering committees, and that special representatives to serve on particular sub-committees should also be appointed by the Institution instead of by invitation from individual companies as previously. This course was made possible by the chief oil companies in the country agreeing to work in this way, in order that nominees might represent and be able to express the views of the industry as a whole.

For these reasons the bulk of the work of the Engineering Standardization Committee is carried out by correspondence and by attendance, either personally or vicariously, at committee meetings of the B.S.I. Documents from the British Standards Institution are received by specific members of the Committee in the following subjects: Mechanical Engineering; Electrical, Chemical, Public Works and Gas Engineering. Each such member is empowered to form sectional committees by co-option either from within or without the Institution for the purpose of discussing subjects of importance to the Industry. They are further responsible for the nomination of individuals to act for the Institution on the B.S.I. Committees. It is significant of the breadth of outlook on the subject that it is agreed where by virtue of no suitable member of the Institution being available to serve on an appropriate Committee, a non-member may be selected to act and to report back.

Along these unobtrusive lines of co-operation with the B.S.I. much valuable work has already been accomplished. Some twenty nominees have served upon different B.S.I. sub-committees as representatives of the Institution. The subjects dealt with have included Pipe Fittings and Pipe Threads; Steam Flanges; Welded Mild Steel Drums; Metal Containers for Inflammable Liquids; Oil-burning Equipment; Furnaces, Ovens and Kilns; Oil-well Cement; Oil-well Casing; Steam-jacketed Pans; Rubber Hose; Tests for Rubber and Rubber Products; and Lightning Conductors. It is not too much to say that without the participation of the Institution it would not have been possible for the deliberations of these B.S.I. sub-committees to have been successfully prosecuted.

Before leaving this question of standards, I wish to allude to the interest taken by the Institution in international standardization. Whilst I do not subscribe to the views of those who regard this conception of internationalization as a mere fantasy to be achieved only at the millennium, it must be admitted that neither one end nor the other of the rainbow has yet been discovered. I am tempted to say that it never will, though "never" is a long time. It seems that it would take a universal dictatorship to make one country or another give up its own established practice in favour of somebody else's. Even when it comes to new tests or equipment, there appears to be an inhibitory force at work preventing agreement on quite simple details. Take the mere instance of the measurement of viscosity in absolute units, which at long length appears to be on the verge of becoming world-wide industrial practice. The essential apparatus is a small glass tube devised and described by Ostwald fifty years ago. The Institution of Petroleum Technologists, the B.S.I. and the A.S.T.M. have severally recorded the shape and dimensions of this tube. British and American are different, and both are different from Ostwald's original. Doubtless the results obtainable are equally accurate, but the fact remains that they are diverse, that they call for separate manufacturing models and even for separate methods of support within a thermostat.

This simple instance shows how difficult it is to obtain international agreement upon standards, even when two countries concerned are so sympathetically united as the U.S.A. and ourselves.

It is our intention nevertheless to pursue every course which may assist towards this desirable end, and to support whatever projects may be

embarked upon for the purpose. Realization of the need for international co-operation in standardization and nomenclature was, in fact, one of the basic reasons for bringing into being the World Petroleum Congress in 1933. For the inception of the Congress, and for always keeping before us this ideal of international understanding and definition, we are greatly indebted to our past-president, Mr. James Kewley, in whose term of office the decision to hold a World Petroleum Conference was taken.

The willingness of the Institution to co-operate cordially with the International Standards Association does not, however, close our eyes to the innate difficulties which have to be overcome. At present the I.S.A. is moving in the direction of agreement upon nomenclature. Much work is being done both through its co-ordination, and individually in different countries, to provide exegeses of the phraseology of petroleum in use throughout the world.

At the same time there are appearing more, and more exact, means of determining the equivalents of arbitrary national scales or the results of localized tests.

Whilst viewing with admiration the efforts which are being made in such directions, I cannot but feel that all exegetical or explanatory methods are likely to be a drag upon true progress towards internationalization. Such methods crystallize differences rather than removing them. The better the translation the less likelihood there is of adopting common phraseology. The more exact the determination of equivalents of different scales of measurement the less chance, there seems to me, of deciding upon a common scale.

It may be, however, that with the continuous changes going on in the petroleum industry and the need in many cases of bringing into being entirely new tests and measurements, the existence of a framework of equivalent terms may assist in the adoption of international standards for the purpose.

One thing will certainly benefit from the tendency towards lexicography. International discussions on matters of technical interest will be mutually more understandable, and therefore more fruitful. That was already apparent at the 2nd World Petroleum Congress in Paris last year. It will become still more so at succeeding meetings.

World Petroleum Congress.

Much has already been said and written regarding the part played by the Institution of Petroleum Technologists in inaugurating the World Petroleum Congress. In that respect I will add thereto only a few self-congratulatory words to the effect that that convention has been given a lasting form, with a permanent Council, and having its secretariat in London. The value of this service of the Institution to the petroleum industry is great. Successive Congresses will serve as monuments to the vision and determination of the Institution, whilst acting as landmarks in the progress of petroleum technology throughout the years. Like other services of the Institution to the industry, this particular one has been given spontaneously, generously and disinterestedly. The only reward which has been asked is opportunity and encouragement to do

greater things in the future. We can scarcely doubt that they will be forthcoming.

As it was not my intention merely to give you a summarized history of the Institution in the past, neither do I propose to forecast in any sort of detail its near or distant future.

I should be falling short in my duty, however, if I did not complete the syllogism of my address by a re-dedication of the forthcoming Institute of Petroleum to the services of the petroleum industry.

What has been accomplished in the past, and what is being done at the present, will surely be done in even greater measure in the future.

"... Thought and faith are mightier things than time can wrong. ..."

On its broader basis the Institute of Petroleum will not fail to give its strength, as the Institution of Petroleum Technologists has done, for the purposes and in the service of the great industry which the Institution helped to found.

I am glad to think that within the Institute will merge the interests of those men of whom Lord Greenway spoke when he occupied this chair just twenty years ago. He said,

> "The Institution was, as you all know, founded with the aim of promoting the co-ordination of the energies of the many classes of experts required for the successful development of the petroleum industry; scientists for the study of its many geological, mineralogical, chemical, physical and other problems; technologists for the examination and solution of the engineering, electrical, shipbuilding, and other problems which also continually arise in connection with producing, transporting and refining petroleum; and financial and commercial experts for providing the capital and finding the most remunerative outlets for its products."

This close co-ordination of the technical and commercial elements in the industry was also deeply at the heart of the Founder-President himself who expressed it on the same occasion as the deliberate aim of those who took part in the foundation of the Institution.

We can look to the future with hope and faith, and I trust with not a little charity. We are pledged to the safeguarding of the professional status of our technologists; but we are also pledged to the co-ordination of their interests with those of whom Redwood and Greenway spoke. I am glad to think we should have had the support of these two great men in the changes we are making in the constitution.

We hope to bring within our fold the economists, the financiers, the administrators, the executives, the distributors and the marketers. If we do that, and if we can weld their strength with that of the technologists for the increased benefit of the petroleum industry which we serve, it will be well done.

SPECIAL GENERAL MEETING.

22nd March, 1938.

A SPECIAL GENERAL MEETING of the Institution of Petroleum Technologists was held at the Royal Society of Arts, John Street, Adelphi, London, W.C.2, at five-thirty o'clock in the afternoon of Tuesday, 22nd March, 1938. The President (LT.-COL. S. J. M. AULD) occupied the Chair.

There were present 46 Members, 9 Associate Members, 2 Associates and 2 Students, a total of 59.

The Secretary (MR. S. J. ASTBURY) read the Notice convening the meeting.

THE PRESIDENT then proposed the adoption of the following Resolutions as Special Resolutions. As the text of the Resolutions had previously been circulated, and most of the members present had their copies in front of them, he would take the Resolutions as read.

RESOLUTIONS.

1. THAT the name of the Institution be changed to "The Institute of Petroleum."

2. THAT the provisions of the Memorandum of Association of the Association with respect to its objects be altered in manner following, that is to say:

(I) By deleting the word "Institution" in line 1 of Clause 3 and substituting therefore the word "Association."

(II) By substituting for subclause (A) of Clause 3 thereof the following new subclause (A), namely:

(A) To enable technologists and others engaged in the petroleum and allied industries to meet and to correspond and to promote, encourage and co-ordinate the study of petroleum and its allied products in all or any of their aspects and to accumulate, extend, increase and disseminate information and knowledge relating thereto and to facilitate the exchange of information, knowledge and ideas on all subjects connected therewith amongst the members of the Association and otherwise and to initiate, conduct, assist and finance investigations and research relating to the occurrence, winning, production, refining, transportation, storage, distribution, utilisation, analysis and synthesis of petroleum or any of its products.

(III) By substituting for subclause (B) thereof the following new subclause (B), namely:

(B) To promote the better education and training of persons engaged in or intending to engage in the petroleum or allied

industries and if thought fit to hold examinations, award certificates, diplomas, prizes or scholarships and to adopt any lawful means conducive to the setting up of a high standard of proficiency and to maintain a high standard of professional conduct among those employed in such industries: provided always that no certificate or diploma shall be issued which does not contain upon the face of it a clear statement to the effect that it is not issued by or under the authority of the Board of Trade or any Government Department or Authority but is issued upon the authority of the Association only.

(IV) Subclause (C) by substituting for the words "or shale oil industry" the words "and allied industries."

(V) Subclause (D) by substituting for the word "industry" the words "and allied industries."

(VI) By inserting therein immediately after subclause (E) thereof the following new subclauses to be called (E) (i) and (E) (ii) respectively:

(i) To establish and maintain a library or collection of books, manuscripts, maps, statistics, drawings, photographs, films, models or other objects relating to petroleum and kindred subjects and to compile, print in any language, publish and distribute the proceedings and reports of the Association and any communications, papers, books or statistics relating to petroleum or kindred subjects.

(ii) To promote the formation of branches, sections or groups of the Association and to co-operate or affiliate with other bodies in any part of the world having objects wholly or in part similar to those of the Association.

(VII) By substituting for the words "The borrowing of any" in subclause (G) the words "To borrow."

(VIII) By inserting therein immediately after subclause (G) thereof the following subclauses to be called subclauses (H) and (I) respectively, namely:

(H) To apply for, invite and accept donations, endowments and gifts of all kinds for the purpose of carrying on or furthering the objects of the Association and either subject to or not subject to any lawful trusts or conditions.

(I) To acquire, improve, manage, develop, sell, exchange, lease, let or otherwise dispose of and deal with all or any property or rights as may be deemed expedient with a view to the promotion of the objects of the Association.

(IX) By substituting (J) for (H) and (K) for (I) in the lettering of the remaining subclauses of Clause 3.

(X) By inserting at the end of Clause 3 thereof the following words:

"In this clause the word 'petroleum' shall be read in its widest sense and shall include all natural and synthetic bitumens and hydrocarbons derived from any source from the lightest gaseous state through the varying densities of liquids to the various solid forms."

3. THAT upon such alteration of the Memorandum of Association being confirmed by Order of the Court and the Registrar of

Companies certifying the registration of an office copy of such Order and a printed copy of the Memorandum as altered pursuant to section 5 (6) of the Companies Act, 1929, the regulations contained in the printed document submitted to the meeting and for the purpose of identification subscribed by the Chairman thereof be and are hereby approved and adopted as the Articles of Association of the Institute in substitution for and to the exclusion of all the existing Articles of Association thereof.

Continuing, the President said that it was a very important occasion, and he did not intend to embellish the proposal that those resolutions be adopted. He had had the opportunity of sending to all concerned a letter embodying his own and the Council's view on the matter.

Mr. E. A. Evans (Member) said that he had very much pleasure in seconding those very important and historic resolutions.

Mr. J. Kewley (Past President), in supporting the motion, said that that was not the time for a speech, but he expressed the hope and surety that the adoption of the Resolutions would mean a greatly enhanced future for the Institution.

The President said that, it having been proposed, seconded and supported that the Resolutions be adopted, he would like to hear if there were any amendments or any questions before he formally put the proposals to the meeting.

Discussion of Resolutions.

Mr. E. H. Cunningham Craig said that, speaking as a founder Member of the Institution, he thought this was rather a sad occasion. He did not want to make a speech about it, although he could have said a great deal. He had read the President's little Memorandum with great interest, and although the President was not, like himself, one of the original Members, he had been a Member for a great many years. There was one thing that struck him about the whole matter, and to him it had come as a shock. He did not happen to be one of the inner circle who knew all that was happening, more or less, behind the scenes, and the thing had come as a bolt from the blue. It was probably the most momentous thing that an Institution of this type could do.

A point to which he wished to direct attention was that the date of the Notice of the Meeting was the 21st February. It would be a very interesting thing to know what proportion of those who had a right to speak or to vote on this subject had had time to receive this Notice and to express an opinion. Perhaps the Secretary could let them know what date the Notices were posted to the various overseas Members—for instance to such places as the Argentine, or to Venezuela, or the East Coast; because if they had not had time to receive the Notices and record a vote, the Institution was weighting a plebiscite very much in favour of those who lived in London. He did not think the Council would desire that, and it

was a question which he thought to be rather important. He asked whether it had been made possible for every overseas Member to record his wish on this matter or not?

THE SECRETARY said that the Notices were posted on the 26th February to members in this country and on the 28th February to overseas members.

MR. L. J. WILMOTH said that in that case it was impossible for them to have received them, and he doubted whether many of the members, and a high proportion of the members, had ever even seen this document; and now they were sitting in London making such a momentous change. He himself thought that it was wrong, fundamentally wrong. (Hear, hear.) He was not talking about the merits of the case; he was leaving that entirely out of it, but they were definitely disfranchising a very large number of the members. All of those present who had been abroad must know that the one accusation that was always heard amongst the actual workers on the fields was that London had too big a say; and he thought if this proposal went through they would have some justification for saying so.

He moved as an amendment: "That this matter be adjourned to give the members of the Institution who reside abroad sufficient time to consider and express their views." He did not know whether anyone would care to second that, but he thought it was a very fair amendment.

MR. S. H. CHAPMAN, in seconding the amendment, asked if members might be told why this proposal was necessary. He wanted to know the why and the wherefore of it, and the assurance that the Institution would not thereby lose its dignity, nor become too much commercialized. Many members did not know why it had been done, and he asked for a debate about it.

THE PRESIDENT said he thought he could answer Mr. Chapman's point there and then. The answer was that the matter had been under consideration by the Council, and by successive Councils of the Institution, over a period of years, and that after it had been actually formulated, that individual letter to which he had referred had been the basis of three successive Council meetings, to which a great deal of consideration as well as a great deal of time of his own, had been given in order that nothing should be done without giving the fullest possible explanation that was within their powers of expression to do. He personally had nothing to add to what had been given in that letter; he could not possibly, without writing a book on the subject, put it into more cogent language.

MR. R. J. BRESSEY said that in view of the President's statement, he wished to support the previous two speakers. He thought it was owing to the members of the Institution that they should receive more information as to what lay behind this move. He had carefully read the explanatory memorandum, and so forth, and it was all in rather vague terminology, if he might be allowed to put it in that way, which told them very little. From discussions he had had with other members there was a quite strong

feeling in that direction, and he thought that if they could be given a little explanation of the real underlying reasons for the changes, it would stand a better chance of being passed with unanimity. As the seconder of the resolution had said, the move was an historic one, and he felt that this step should not be taken by the Institution without the fullest discussion, and revelation of the motives which lay behind it.

MR. A. F. DABELL asked that progress be not delayed by the point raised that foreign members had not had time to consider the matter.

As past Chairman of the Roumanian and Trinidad Branches he knew the members were for progress. Moreover, last year when the Branch Chairmen were in London he had put the point to them whether they were satisfied to remain in a "third floor back." Invariably, when pressed, they had declared "You must go ahead."

To do that they had to broaden the basis of the Institution, and on that principle he had worked and for the last twelve months had been making continual visits to London to wade through the details now submitted.

MR. G. H. COXON said that the question seemed to him to be one affecting fundamentally the relations between the Institution and its Council. If the members of the Institution could not trust the Council to get on with a job like this, when the Council saw fit to take a certain course which they considered was in the interests of the Institution, then what were the functions of the Council? The Council had been sitting on this matter for about two years, and it had been debated backwards and forwards. It was necessary to move with the times. The industry was growing, and he for one certainly supported the Resolutions.

PROFESSOR A. W. NASH asked if he might raise one point which he thought they had all forgotten. That was that Lord Cadman, when he was President, at the Dinner in 1936 mentioned in his speech that the matter was being considered. Lord Cadman had put forward the reasons on that occasion, most of which the speaker had forgotten, but he remembered one which was mentioned, and that was that he considered that the sale of the product was in a way just as important as its production. He therefore felt that, apart from any information which might have been given officially by the Secretary, every member of the Institution should have known about it, even if he were not present at the Dinner, if he had read the speeches which were reported in the *Journal* at that time.

MR. J. KEWLEY said the members must be very careful to look at the matter in a realistic way, and see that they had a correct picture. He had taken a very great interest in this question since its inception, and he felt that strongly with Mr. Dabell that an Institution must progress, otherwise it was going to die. There was no such thing as a static life in this world; one either went ahead or one went backwards; and once one went backwards, one went backwards a great deal more quickly than one could ever go forward. The Institution's curve of membership, it was true, was going up, but not quite at such a steep incline as it had previously. The Institution was known very largely in the world by its *Journal*. The

Journal of the Institution was becoming of more and more importance. The *Journal* was the one thing that the Institution must maintain in order to keep its reputation up to date. The *Journal* was well spoken of in every country he had visited; but the *Journal* meant more money. There were only two ways in which they could raise more money, and that was either by raising the subscriptions of the existing members, or by extending their membership.

There was no reason, as Mr. Dabell had said, why a person who was interested in the accounting side of the industry should not belong to an association of technical men. He at least did not contemplate the possibility of the Institution becoming commercialized. The Fellowship of the Institution would still remain a closed avenue to the members who had not got the same qualifications as some of the present members had, but the reconstitution would enable them to admit a very large number of men holding responsible positions in the industry into the Institution—not necessarily technical men, but not by any means salesmen—managerial men who might not have the qualification of five years in a technical position in the industry. He submitted that it was perhaps not the most important job that one could hold to have a qualification of five years in a technical position in one particular field; and he felt that by extending their membership in that carefully controlled way they could bring in a very largely increased income, and enable the Institution to go on with its excellent work, maintaining its *Journal* up to standard. That was the picture which he thought the members should have in view. (Hear, hear.)

Dr. A. E. Dunstan wished to associate himself with what Mr. Kewley had said. It was preposterous and ridiculous for the idea to get round that there was something hole-and-corner about this matter, something behind the scenes. There was nothing behind the scenes. The Institution's own Council, elected on quite democratic lines, had given to this project the most careful and intimate consideration for a long, long time. There was a very obvious answer: Refuse to re-elect your Council, but in the meantime give them the credit of a certain amount of discretion and common sense.

Dr. E. R. Redgrove said they were proposing to call themselves the "Institute of Petroleum," and thereby to bind together in one body all those who were interested in petroleum for their livelihood. Being a scientist, he much resented the slight which was apparently cast upon a salesman, because he thought that the salesman of to-day, if he was worthy of his name, did not sell on the talk which prevailed years ago, but sold on service. He must know the article he was selling, and see that it was being used in the right way. For that reason he thought that salesmen should not be debarred from membership of the Institute of Petroleum, and from the opportunity of learning more about the article which they were offering to the public.

The President's letter clearly outlined the points in favour of the change and surely the 700 letters which had been sent out had been received by the majority of the people to whom they were addressed. He asked whether there had been any written objections to the proposed change in

name and constitution; if there were no such objections it could be assumed that there were none forthcoming.

Mr. R. J. Bressey appealed to those who spoke for the Council not to regard anybody who raised questions as a sort of pariah. They were there as representing the membership of the Institution, and they wanted to be told what was happening, and he did not think that was any reflection on the members of the Council at all. After all, there was a little analogy which might be drawn with Parliament and the Executive. The Executive did not expect to get all its Bills through without any questioning in Parliament, and it surely was not unreasonable for the humble rank and file to express a few thoughts about the proposal. It was not a lack of confidence in their Council. They only wanted to learn and to be told, and he thought Mr. Kewley had gone a considerable way towards meeting the point which members had raised. He had told them a little about the objects which the Council had in mind, and that therefore to some extent answered their questions. He felt, however, that those who had taken the trouble and the time to come to the Meeting should not be regarded as questioning the good faith of the Council.

Mr. G. W. Furniss said that although he anticipated on that occasion a fair amount of opposition to the change in name, he had hardly expected that the members would not have taken a rather broader view of this particular matter. First, with regard to the name of the "Institute of Petroleum," they had become a very much larger Institution during the last seven years, with much wider interests. When they were, as several members had said, a purely scientific Institution, a very large number of men in the industry were debarred from membership. He thought by that procedure they were debarring some of the very best brains in the industry. He realized that certain members, regarding it purely from the scientific point of view, would prefer to retain the scientific name by which they were associated with the Institution; but, after all, the "Institute of Petroleum" covered a very wide area; it took in practically every branch of the petroleum industry; and he thought that was the object of this change of name.

Mr. L. J. Wilmoth said he thought there had been some misunderstanding on the point he had raised. He had only raised one question. He had not challenged anything with regard to the change of name, or the idea; he had not said one word on it. What he did emphasize was this, that the Notice the Council had given for such a big change was much too short, and that they had not given a large number of members of the Institution, who had as much right as any of them sitting there to express a view, any opportunity to do so. His amendment was that the consideration of this question should be postponed sufficiently long to give every member of the Institution a chance to express his views. That it had been discussed in Council was obvious, and no doubt the Council felt there was very good reason for making the change, otherwise it would not have come along; but, having spent most of his life abroad, he

felt that those who work abroad should be given a full chance with those who work in this country. He was not raising any question about the desirability of changing their name or anything else, but he thought the consideration of the matter should be postponed sufficiently long, and that the recommendations should have been sent out in such a form that all overseas members had an equal opportunity with the people at home. That was the basis of his amendment, and he thought it was a question of ordinary equity and justice. The President's motion in front of the meeting did not show equity towards the Institution's overseas members.

MR. C. I. KELLY thought there was not much difference in the actual view between the proposers and the amenders of the proposals. He thought the difference lay in the method, the procedure to be adopted. Surely it was clearly laid out in the Articles of Association, and if the President could give the members an indication that the procedure was valid, the matter went through. The question of confidence in the Council's functions would be the deciding factor.

THE PRESIDENT, having asked the Meeting whether anybody else wished to speak, and there being no reply, said that before putting the amendment to the Meeting he would like first of all to assure Mr. Kelly that every single action which had been taken had been taken with the closest attention to every detail, and was in accordance with all the Articles and the By-Laws of the Institution of Petroleum Technologists. He referred to Paragraph 37 of the Articles of Association where it is said :

> "No Member, Associate Member, Student, Associate or Honorary Member, not having a registered address within the United Kingdom, shall be entitled to any notice, and all proceedings may be had and taken without notice to such Member in the same manner as if they had had due notice" (Article of Association, 37).

Actually, of course, as you have heard, all these Notices have gone to the members abroad ; and in that connection the members would be interested to hear that of the 700 going to people in this country, and probably the other 700 going to people within very easy reach of this country, they had had only one single letter in connection with the change, and that referred to the suggestion that it should be "Institution" instead of "Institute."

The President said that he personally was a little disappointed about the work which had been done in this connection being at the last moment called into question. Although he could not do more than to refer to the printed documents in front of the Meeting, from the speeches by Lord Cadman and others, from what they had heard about the Council's good relations between the Chairmen of the branches and the visiting members of the Branches and so on, it had been common knowledge to those who had been actively interested in the doings of the Institution as a whole that this change was contemplated. He did not think it had occurred to any member of the Institution that this question of acting in any way at short notice, or of disfranchizing anybody, or of not taking proper care or consideration, was contemplated in any way. He had come there prepared to answer questions regarding the anticipated machinery for making the change, to clear up the thought given to it, and give the reasons therefor.

As he had said before, he had not been able, and could not even now, express more completely or with greater clarity the reasons for the changes which he had already given in the circular letter; but he would like to point out a very important, and perhaps the main, reason why one should make this change. Surely, with the advent of new conditions in the petroleum industry, a large number of men who were as keenly interested, who were as intelligent, as those who were actually technical men in the petroleum industry, should be allowed to become members. It was not right that they should be excluded from this Institute, as he hoped for their sakes it would become, and the idea that they were broadening it out to the basis where they were not attracting men who were going to do them credit, he thought was utterly wrong. They would have with them the statisticians, the accountants; they would have the whole of the distribution and administration staffs, who would actually be eligible for membership under these conditions. Every consideration had been given to the retention of the professional status of the Institute, at the same time, by the formation of a new class, which would have a definite status equal to that of a Fellow. How that would be implemented he would be prepared to be heckled about, but before putting the amendment to the Meeting regarding the postponement of the question, he would be glad to have the opportunity of making that quite clear. He would formally put the amendment to the Meeting.

MR. S. H. CHAPMAN, after having heard Mr. Kewley's explanation asked permission to withdraw his seconding of the amendment. He did not wish to force a vote and asked if the proposer would get another seconder.

MR. L. J. WILMOTH said that he had expressed what he wished to say and would not ask for another seconder.

MR. S. H. CHAPMAN suggested that in those circumstances, if he withdrew his seconding of the amendment, that would dispose of the matter. (Applause.)

THE PRESIDENT said that in that case it would be in order for him to put the original proposition to the Meeting.

PROFESSOR J. S. S. BRAME asked if on a point of order he might raise the question whether all the ladies and gentlemen present were members of the Institution?

THE PRESIDENT answered that he was informed that there was one lady present, who was a visitor, whom they were very glad to welcome.

The President then formally put the proposals to the Meeting. He said that the resolutions had been proposed and seconded and supported, and on a vote of hands declared the resolutions carried, with one dissentient.

The President then formally signed the document.

He went on to say that before closing the Meeting he would like to add that in regard to Fellowship particularly, there must be a lot of con-

sideration given as to how that was to be treated, and as to how they would stand as members of the Institute themselves at present. The full machinery had not yet been decided upon, but he could assure the Meeting that not merely close consideration, but every consideration, would be given to existing members, and that, in the words of a Minute of the Council, there would be a liberal interpretation of the requirements; because it was important that they did no injustice to present members of the Institution in any change which was made.

THE PRESIDENT then declared the Meeting closed.

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

ANNUAL GENERAL MEETING.

22nd March, 1938.

THE Twenty-fifth Annual General Meeting of the Institution was held at the Royal Society of Arts, John Street, Adelphi, London, W.C.2, at 6 p.m. on Tuesday, the 22nd March, 1938. The Chair was taken by the President (LT.-COL. S. J. M. AULD).

The Secretary (MR. S. J. ASTBURY) read the Notice convening the Meeting and the Reports of the Auditors on the Balance Sheet of the Institution and the Accounts of the Benevolent Fund.

The Minutes of the Twenty-fourth Annual General Meeting, held on 9th March, 1937, were read, confirmed and signed.

THE SECRETARY announced that as the result of the Ballot the following had been elected members of the Council: MR. A. FRANK DABELL, PROF. V. C. ILLING, DR. E. R. REDGROVE, MR. W. J. WILSON and MR. C. W. WOOD.

It was agreed that the list of Honorary Members, Members, Associate Members, Students and Associates elected or transferred between 1st January and 31st December, 1937, be laid on the table.

THE PRESIDENT then proposed that the Annual Report of the Council for the year 1937, together with the Accounts and Balance Sheet as at 31st December, 1937, be adopted.

MR. G. H. COXON (Acting Chairman of the Finance Committee) seconded the adoption of the Annual Report and Accounts, and said that he would take the opportunity of adding a few comments on the financial aspect. He considered it was important that the members of an Institution of this character should appreciate how the finances were being handled. Properly speaking, it was the function of Mr. Dalley, the Chairman of the Finance Committee, to deal with this aspect. Mr. Dalley, however, was abroad, and he (Mr. Coxon) had been asked by the Council to deputize for him.

There were only two points that called for comment. The first was the all-round reduction of expenses which had been attained during the year. This was remarkable, because there were very few technical societies which had been able to carry on during the past year with reduced expenses. The tendency was rather the other way. The second point

was a satisfactory increase in income from various sources. The net result was that at the end of the year there was a very favourable balance of £719. Some people might criticize the Finance Committee by saying that an Institution of this character ought not to have a surplus, but should use its money for its members. However, the Institution had a very heavy year in front of it; they were going to move into new premises, and those premises had to be re-furnished. He considered it was prudent for the Finance Committee to have money in hand, ready to meet any expenditure which might arise in that connection.

Mr. Coxon said that he would like to pay a tribute to the great amount of work which had been carried out by the President during the past year. In preparing the matters discussed at the previous Special General Meeting, there had been a vast amount of discussion, drafting and re-drafting at meetings of the Council and Committees. The President had personally taken a great share in this work.

Speaking on behalf of the Finance Committee, Mr. Coxon also paid a tribute to the work of Mr. Astbury. Although their Chairman was Mr. Dalley, the detailed work of looking after their income and expenditure was carried out by the Secretary, to whom the members owed a debt of gratitude for the work he had done.

He had pleasure in seconding the Resolution put forward by the President.

THE PRESIDENT then asked whether there were any comments on the Council's Report.

CAPTAIN W. H. CADMAN said that he noticed that, in the reference to the forthcoming Scottish Conference, mention was made only of Mr. Conacher and himself. There were, in point of fact, two Honorary Secretaries of the Scottish Conference—Mr. Conacher and Dr. Hugh Nisbet. He would like Dr. Nisbet's name to be included in the Report.

THE PRESIDENT replied that he would be very pleased to see that this was done.

No further questions being asked, the adoption of the Report and Accounts was put to the meeting and carried unanimously.

On the proposition of MR. L. J. WILMOTH (Member), seconded by MR. W. H. HOWE (Member), Messrs. Price, Waterhouse & Co., were re-elected Auditors for the ensuing year.

THE PRESIDENT then formally proposed the adoption of the resolution, Item No. 6 on the printed Agenda, arising out of the Special Meeting, viz.: "To consider and if thought fit to pass with or without amendment the following Resolution, namely:

"That upon the happening of the events referred to in the third paragraph of the Special Resolutions passed at the above-mentioned Special General Meeting preceding this Meeting, By-Laws numbered 1 to 16 on the following pages be and are hereby approved and adopted as a part of the By-Laws of the Institute in substitution for and to the exclusion of the existing By-Laws numbered Sections I, II, III and Section VI, paragraphs 1 to 7 inclusive, the remainder of the existing By-Laws to remain in force for the time being."

DR. A. E. DUNSTAN seconded the resolution.

The Motion was put to the meeting and carried.

THE PRESIDENT announced that he would have a better opportunity subsequently of enlarging on the reference he was now making, but he was sure members would be interested and glad to hear that at the Council Meeting that afternoon it was unanimously recommended and adopted that the Redwood Medal be awarded to Dr. Dunstan. (Applause.)

THE PRESIDENT then declared the Meeting closed.

TWENTY-FOURTH ANNUAL REPORT.

1937.

THE Twenty-Fourth Annual Report of the Council covering the activities of the Institution during 1937 is presented for the information of the members.

MEMBERSHIP.

The changes in membership which have occurred during 1937, and the total membership on 31st December, 1937, are summarized in the Table below.

	Total Dec. 31, 1936.	CHANGES DURING 1937.							Total Dec. 31, 1937.
		New.	Transferred to.	Resigned.	Deceased.	Removed.	Transferred from	+ or −	
Hon. Mems.	18	3	—	—	—	—	—	+ 3	21
Members	676	57	12	16	6	8	—	+39	715
Assoc. Mems.	503	37	18	9	2	9	12	+23	526
Students	110	15	—	5	—	20	18	−28	82
Associates	97	6	1	2	—	2	1	+ 2	99
	1404	118	31	32	8	39	31	+39	1443

The Council has noted with regret a gradual fall in the number of Student Members which has been taking place since 1930. With this exception the membership of the Institution exhibits a steady but satisfactory growth.

The Council has to record with deep regret the decease of the following members during 1937 :

	Date elected.	Class of Membership.
BOWMAN, T. SUTTON	1924	M.
GALLOWAY, W. J.	1928	A.M.
GARRETT, T. R. H.	1914	M.
HANNAN, S. M.	1934	A.M.
MANFIELD, W. HARDY	1914	M.
SPENCER, THEODORE	1914	M.
TAKAKUWA, T.	1920	M.
WAERDEN, H. VAN DER	1927	M.

Major T. R. H. Garrett and Mr. W. Hardy Manfield were Original Members of the Institution. Major T. R. H. Garrett was a member of the Council from 1929 until his decease.

The Council also has to record the deaths during the year of two former members of the Institution : M. Paul de Chambrier (awarded Redwood Medal in 1925) and Mr. C. B. McKeever (formerly Rosenplaenter) a Founder-Member.

Honours.

His Majesty King George VI conferred a Barony of the United Kingdom upon Sir John Cadman, G.C.M.G., D.Sc., D.Litt., D.Eng. (President 1916–1917 and 1935–1937).

Lt.-Col. H. C. B. Hickling, D.S.O., M.C. (Member), received the honour of Commander of the Order of the British Empire.

Prof. Henri Weiss (Associate) was nominated Chevalier of the Légion d'Honneur.

Representation on Other Bodies.

The Institution has been represented during 1937 on the following bodies :—

The American Society for Testing Materials. Dr. A. E. Dunstan.
The British National Committee of the World Power Conference. Dr. A. E. Dunstan.
The Institution of Mechanical Engineers Organizing Committee of the General Discussion on Lubrication. Mr. E. A. Evans.
The British Standards Institution Petroleum Industry Committee. Col. S. J. M. Auld, O.B.E., M.C., Prof. J. S. S. Brame, C.B.E., Dr. A. E. Dunstan, Mr. B. J. Ellis, Dr. F. H. Garner, Mr. J. Kewley and the Secretary.
The International Standards Association Conference in Paris, June, 1937. Dr. A. E. Dunstan, Dr. F. H. Garner, Mr. J. Kewley, Dr. P. Spielmann, Mr. C. W. Wood, and the Secretary.
Second World Petroleum Congress, Organizing Committee. Dr. A. E. Dunstan, Mr. J. Kewley, and the Secretary.
Permanent Council of World Petroleum Congresses. Lt.-Col. S. J. M. Auld and Mr. Dewhurst.
South Wales Advisory Committee on Technical Education. Mr. W. C. Mitchell.
The Advisory Board of the Department of Oil Engineering and Refining, Birmingham University. The President.
The Diesel Engine Users Association. Prof. J. S. S. Brame, C.B.E., and Dr. F. H. Garner.
The Power Farming Development Board of the Society of Motor Manufacturers and Traders. Dr. W. E. J. Broom and Mr. L. J. le Mesurier.
Congres de Chimie Industrielle. Dr. A. E. Dunstan.
XVIIIth International Geological Congress (London) 1940, General Committee. Mr. T. Dewhurst.
A.P.I. Meetings in Chicago, November, 1937. R. Stansfield and D. G. Smith.
C.F.R. Committee Meetings. R. Stansfield.
Permanent International Association of Road Congresses. Dr. P. Spielmann.

Benevolent Fund.

On the occasion of the Coronation of King George VI and Queen Elizabeth the Council issued a special appeal for the Benevolent Fund of the Institution. The booklet issued in connection with this appeal contained a list of Donors to the Fund from the date of its inception (1929) and a list of typical cases which had been assisted by the Benevolent Fund.

The Council is pleased to record that a generous response was made to this appeal, and wishes to thank all those members who contributed to the Capital Fund or forwarded subscriptions for current purposes. Donations to the Benevolent Fund were received during 1937 from :

Adams, A. C.	Beavan, A. M. E.	Brodie, N. M.	Clement, L.
Andrews, B. G.	Bell, O. A.	Bushnell, G. H. S.	Cole, F. A. J.
Auld, S. J. M.	Blakiston, H.	Cambi, V.	Cox, A. W.
Ballardie, A. W.	Bolton, R. P.	Cameron, I.	Crichton, R.
Barrett, G. M.	Brame, J. S. S.	Chambers, A. E.	Dalley, C.
Barrington-Brown, C.	Bressey, I J.	Charlton, A. E.	Downs, W. W.

Dunkley, G. W.
Dunstan, A. E.
Edeleanu, I.
Ellis, B. J.
Evans, R. J.
Fay, E.
Ferguson, B. C.
Frewing, J. J.
Garner, F. H.
Gluckmann, B.
Gould, G. C.
Graham, W. R.
Griffiths, S. M.
Hamilton, A.
Hamilton, L. B.
Henson, F. R. S.
Higgs, P. G.
Hill, C. V.
Hills, S. R.
Jackson, J. S.
Jameson, J. A.
Jennings, J. C.
Kamen-Kaye, M.
Kelly, M. E.
Kewley, J.
Lepper, G. W.
Machadyen, W. A.
Mackenzie, W. L.
Mahdi, S. J.
Masters, J. S.
McCreath, T. T.
McGavin, W. K.
McKilligan, R. S.
Le Mesurier, J. L.
Mitchell, J. P.
Mitchell, R. G.
Moon, C. A.
Moore, H.
Nash, A. W.
Parr, R. W.
Parrish, J.
Pearson, B. C.
Perks, A. J.
Porter, P. N. D.
Purdie, A. C.
Purves, A. R.
Redgrove, E. R.
Richards, G. A.
Richardson, D. B.
Sams, C. E. R.
Samuel, D. L.
Sargeant, G. F.
Schlumberger, M.
Smallwood, W.
Spielman, P. E.
Stokoe, E.
Strickland, A. F.
Taitt, G. S.
Taylor, T. M.
Thole, F. B.
Thompson, A. Beeby.
Tullett, G. V.
Wade, A.
Walsh, D. M.
Walter, G.
Waterman, H. I.
Wood, C. W.
Wood, N. E.
Zublin, J. A.
Shell Marketing Company, Central Laboratories.
Oil Industries Club.

The audited Statement of Accounts of the Benevolent Fund for the year 1937 is given below. The Balance at the end of the year on the Benevolent Fund Account was £654 5*s.* 7*d.* The Council decided to invest a portion of this and regard it as a Capital Fund. Accordingly, a sum of £528 17*s.* was invested during January 1938 in £600 (nominal value) 3% Local Loans.

Finance.

The audited Revenue Account for 1937 and the Balance Sheet as at 31st December, 1937, are given below. The accounts call for little comment. Most of the items of expenditure were lower in 1937 than in 1936, and the items of income were higher. The result is a balance of £719 18*s.* 1*d.* transferred to the Balance Sheet.

It will be noted that the grants to the Branches have been shown in detail on the Revenue Account, in lieu of an item showing the total expenditure on the Balance Sheet only. The unexpended Balance of £75 4*s.* 4*d.* in the Branch Fund on 31st December, 1936, has been brought into the Revenue Account.

The special item for Legal Expenses, £80, is mainly in connection with the revision of the Memorandum and Articles which has been taking place.

Meetings of the Institution.

Seven General Meetings of the Institution were held in London during the year. All these meetings were held in the Lecture Hall of the Royal Society of Arts by courtesy of the Council of that body. The subjects of the Papers presented and their authors are given below.

Date.	Subject.	Author.
Jan. 8th.	"Modern High-Duty Aero Engines and their Fuels."	F. R. Banks.
Feb. 9th.	"The X-Ray Examination of Paraffins."	Dr. A. Muller.
March 9th.	Annual General Meeting.	
May 4th.	Conference on Deep Drilling Problems.	W. E. V. Abraham, Dr. J. T. Evans, G. F. Wilson, G. W. Colvill and W. M. Frame.
June 8th.	"Synthetic Products from Petroleum."	Dr. G. Egloff.
Nov. 9th.	Discussion on De-Waxing.	A. W. Nash, T. G. Hunter, M. Ba Thi, B. Engel, E. C. H. Kolvoort, and others.
Dec. 14th.	"The Microscopical Examination of Crude Petroleum."	J. McConnell Sanders.

The average attendance at these meetings was 78, as compared with an average attendance of 67 at the meetings held during 1936.

In addition to the above meetings, the Institution participated in a Joint Meeting organized by the Institution of Automobile Engineers on 2nd March, 1937, at which the subject of "Research in Relation to the Motor Vehicle" was discussed. A Paper by Dr. F. H. Garner on "Fuels and Lubricants" was presented to this Joint Meeting.

The October General Meeting of the Institution was not held. In its place the Institution participated in the General Discussion on Lubrication organized by the Institution of Mechanical Engineers, and held at the Central Hall, Westminster, from 13th to 15th October, 1937. Mr. Harry Ricardo, F.R.S., Hon.M.Inst.P.T. was one of the General Reporters for Group II of the General Discussion—"Engine Lubrication." Lt.-Col. S. J. M. Auld, and Mr. E. A. Evans, were General Reporters for Group III—"Industrial Applications."

Branch Lecture.

Dr. G. Egloff accepted the invitation of the Council to deliver the first Branch Lecture of the Institution in June 1937. The subject of the Lecture was "Synthetic Products from Petroleum." The Lecture was delivered in London on June 8th; in Manchester to the Members of the Northern Branch on June 9th; and in Swansea to the Members of the South Wales Branch on June 11th. It was subsequently published in the November *Journal*.

Annual Dinner.

The Nineteenth Annual Dinner was held at the Connaught Rooms on Friday, 8th October, 1937, and was attended by over 200 members and their guests. In the absence of the President, the Chair was taken by Sir Thomas H. Holland, K.C.S.I., K.C.I.E., F.R.S., Hon.LL.D. The toast of "The Institution" was proposed by Sir Henry T. Tizard, F.R.S. Prof. A. W. Nash, M.Sc. (Vice-President), proposed the toast of "The Guests," to which Col. L. Pineau, Prof. Dr. Ubbelohde and Ir. J. H. C. de Brey responded.

Standardization.

A considerable amount of work has been carried out during the year by the Sub-Committees of the Chemical Standardization Committee, and revisions of several tests have been prepared. An account of this work will be given in a separate Report. The various Sub-Committees have been in close touch with the A.S.T.M. and the C.F.R. Committee in the United States.

The Institution has also collaborated with the British Standards Institution in the work of international standardization of methods of test and nomenclature carried out by I.S.A. Committee 28. The Institution has acted as secretariat of four of the technical committees.

Publications.

The Journal.

Vol. XXIII of the *Journal* was published in twelve monthly parts, and contained 16 Papers read at General Meetings of the Institution in London, 6 Papers presented at meetings of the Branches, 23 contributed Articles and 1502 Abstracts of technical literature and patents.

By grouping together Papers on related topics, it was possible to devote four issues of the *Journal* to special subjects, viz. "Geophysics," "Aero Engines and Fuels," "Deep Drilling" and "De-Waxing" respectively.

"*Petroleum Technology in 1936.*"

"Petroleum Technology in 1936" was published in July 1937. It was approximately twenty per cent. larger than its predecessor of the previous year, and considerably more space was allotted to the section dealing with Alternative Fuels. The main portion of the book, however, as in previous years, was concerned with reviews of the different sections of petroleum technology.

The grateful thanks of the Council are tendered to the individual authors whose contributions made up the book.

Second World Petroleum Congress.

The Second World Petroleum Congress was held at the Maison de la Chimie, Paris, from June 14th to 19th, 1937. The Congress was organized by the Association Française des Techniciens du Pétrole, and was attended by over 1500 participants.

Mr. T. Dewhurst, Past President and President of the First World Petroleum Congress, opened the Inaugural Session on Monday, June 14th, and handed over the Presidency of the Congress to Colonel L. Pineau, Hon. M.Inst.P.T. Mr. T. Dewhurst and Lt.-Col. S. J. M. Auld were subsequently elected members of the Permanent Council of World Petroleum Congresses.

H.M. Government appointed the following as delegates to the Congress: Lord Cadman (Chief Delegate), Mr. F. C. Starling, Mr. T. Dewhurst, Dr. A. E. Dunstan, Mr. J. Kewley, Dr. F. S. Sinnatt, Mr. G. W. Lepper and Mr. S. J. Astbury.

The Congress was honoured by the presence of M. Lebrun, President of the French Republic, at the afternoon session of Monday, June 14th, when M. Henri Weiss delivered an address on the Scientific Problems of the Petroleum Industry.

Lord Cadman addressed the members on the occasion of the Official Banquet on Tuesday, June 15th.

Among those who acted as Chairmen of the various Sectional meetings of the Congress were: Lord Cadman, Dr. A. E. Dunstan, Mr. J. Kewley, Mr. Ashley Carter and Mr. C. A. P. Southwell.

The total of British participants (including ladies) was over 100.

The Council of the Institution acted as the National Committee for Great Britain and the Empire, and was responsible for arranging the presentation

of Papers from British countries. The following nineteen Papers were presented to the Congress through the intermediary of the Institution :—

"Oil Prospecting in Great Britain." The Anglo-Iranian Oil Company (presented by Mr. C. A. P. Southwell).
"Petroleum and Natural Gas in Canada." G. S. Howe.
"Recent Advances in the Search for Oil in Australia." Dr. A. Wade.
"Progress Report on Bahrein Island." J. P. McCulloch.
"General Description of the Iranian Fields." Anglo-Iranian Oil Company.
"Micro-petrographic Methods as an Aid to the Stratigraphy of Chemical Deposits." W. Strong.
"Magnetic and Gravimetric Measurements in Eastern England." Dr. J. H. Jones.
"A Seismic Reflexion Survey in Eastern England." Dr. J. H. Jones.
"The Thixotropy of Mud Fluid." A. Reid.
"Multistage Separation of Oil and Gas." C. J. May.
"Condition of Lubricating Oil after Use in High-Speed Oil Engines." A. T. Wilford.
"A Chart for the Estimation of Viscosity Index from Centistokes." Dr. F. H. Garner and Mr. E. Hardiman.
"Viscosity Temperature Relations of Hydrocarbons." Dr. E. B. Evans.
"Knock-Rating of Gasolines and their Chemical Composition." Dr. F. H. Garner and Dr. E. B. Evans.
"Petroleum in Persia in Antiquity and the Middle Ages." Dr. L. Lockhart.
"Standardization of Tests for Bituminous Emulsions." Dr. F. H. Garner.
"The Use of Bitumen in the Electric Cable Industry." S. Beckinsale and A. King.
"Volume Correction Tables in the Commercial Measurement of Liquid Petroleum." H. Hyams.
"Standard Weights and Measures." I.P.T. Committee on Measurement of Oil in Bulk.

In addition to the above, a large number of Papers were presented by members of the Institution resident in non-British countries.

A total of 430 Papers presented to the Congress, with the Reports of their discussion, will appear in the five volumes of *Proceedings* now in course of publication.

During the week of the Congress a successful series of visits and functions were arranged, including the Official Banquet, a Reception at the Chamber of Commerce and an evening at Versailles.

The Council offers its warmest congratulations to the Association Française des Techniciens du Pétrole, and to all those responsible for the details of organization, upon the success which attended the Second World Petroleum Congress.

Permanent Council of World Petroleum Congresses.

At the Final Plenary Session of the Congress the participants confirmed the appointment of a Permanent Council which would be responsible for safeguarding the interests of World Petroleum Congresses between its successive meetings.

The membership of the Permanent Council is as follows :

Col. L. Pineau, President.
Prof. P. Erculisse (Belgium).
C. Bihoreau and S. Scheer (France).
Prof. L. Ubbelohde (Germany).
S. J. M. Auld and T. Dewhurst (Great Britain).
J. H. C. de Brey (Holland).

Prof. S. Pilat (Poland).
Prof. L. Mrazec (Roumania).
Dr. G. Egloff and W. P. Haynes (U.S.A.).

The Secretariat of the Permanent Council was entrusted to the Institution of Petroleum Technologists, and the Secretary of the Institution was appointed Secretary of the Permanent Council.

A permanent organization for future Congresses was thus created. Meetings of the Council have been held in London on October 8th, 1937, and in Paris on January 22nd, 1938. At the latter meeting the Permanent Council accepted the invitation of the Deutsche Gesellschaft für Mineralölforschung to hold the Third Congress in Berlin in May or June 1940.

Awards.

The two scholarships of £40 each, tenable by Students of the Institution at the Universities of London and Birmingham for the year 1937–38, were awarded to G. E. Higgins (Royal School of Mines) and V. G. Norris (Department of Oil Engineering and Refining, Birmingham University) respectively.

The Redwood Medal of the Institution was presented to Mr. Harry Ricardo, F.R.S., by the President on the occasion of the Annual General Meeting on March 9th, 1937.

Honorary Membership of the Institution has been conferred by the Council upon :

Sir William Bragg, O.M., K.B.E., F.R.S., during the tenure of his office as Director of the Davy-Faraday Research Laboratory of the Royal Institution.

Sir Henry T. Tizard, K.C.B., F.R.S., during the tenure of his office as Rector of the Imperial College of Science and Technology.

Dr. Hasan Sadek Bey, Ph.D., during the tenure of his office as Director-General of the Survey and Mines Department, Egyptian Government.

Mr. A. H. Nissan, B.Sc. (Birmingham University), was awarded the Student's Medal and a prize of £10 presented by Mr. T. C. J. Burgess.

Mr. E. N. Tiratsoo (Royal School of Mines) was awarded a prize of £5 for a thesis submitted for the Student's Medal.

Research.

Two grants were made during the year from the Research Fund of the Institution, viz. :—

To Dr. G. M. Dyson, Ph.D., F.I.C., F.C.S., M.Inst.P.T., Loughborough Technical College, a grant not exceeding a total sum of £100, in aid of a research to investigate the effect of metallic detritus on the oxidation of mineral lubricating oils. Of this total £62 12*s.* 9*d.* had been expended at the end of the financial year.

To the British Electrical and Allied Industries Research Association, a grant of £25 in aid of investigations on the Creep and Corrosion of Steel at High Temperatures. A similar grant has been promised for 1938. The major portion of this research work is being carried out at the National Physical Laboratory. A large amount of data on carbon steels and on molybdenum and complex molybdenum steels has been furnished in reports received by the Institution Library from the Association. These reports are available for consultation by the members.

Work has been continued at the Department of Oil Engineering and Refining, Birmingham University, under the direction of Prof. A. W. Nash, on research on "Porosity-Permeability Relationships." A Paper incorporating the preliminary results of this work will be published in the *Journal* during 1938.

The two Committees of the Council previously known as the "Research Fund Committee" and the "Cancer Research Committee" were amalgamated in September 1937, and became the "Research Committee" of the Council. Mr. J. Kewley, Past-President, is Chairman of the Committee.

Library.

During the past year 403 books were loaned to members, as compared with 381 during 1936. In addition, a large number of technical inquiries and requests for information concerning technical publications have been dealt with by correspondence or telephone. Members residing outside the London area are taking advantage to an increasing extent of the facility of borrowing books and periodicals from the Library by post.

A considerable number of photostat copies of extracts from books and periodicals have also been supplied on payment of the appropriate charges.

As many members are unaware of the extensive range of periodicals taken in the Library, a list of 131 periodical publications regularly received has been prepared, and is available on request. In almost all cases the originals of the Abstracts of articles (excluding patent specifications) which appear in the *Journal* may be consulted in the Library.

The Council wishes to express its thanks to the various Government departments, authors and publishers who have generously presented their publications to the Library. In all cases these have been reviewed or noticed in the monthly *Journal*.

Conference on Oil Shale and Cannel Coal.

The organization of a Conference on Oil Shale and Cannel Coal to be held in Glasgow in June 1938 was initiated by the Council during the latter part of 1937. The Conference has received the patronage of Ministers of H.M. Government and the support of civic and educational authorities in Scotland and of numerous scientific, technical and industrial interests.

The Council expresses its thanks to Captain W. H. Cadman, Mr. H. R. J. Conacher, Dr. H. B. Nisbet, and to all the members of the Scottish Organizing Committee for their valuable co-operation and assistance in the work of completing the arrangements.

Branches.

The Branches of the Institution in Burma, Iran, Roumania, South Wales, Trinidad and the Northern Branch have been well supported by members of the Institution locally. Reports of their activities will be published in the *Journal*.

The Council was glad to welcome a number of American members in London in June, 1937, when they were visiting Europe for the Second World Petroleum Congress.

The Annual Dinner of American members of the Institution was held in Chicago on November 10th, 1937, and was well attended. Dr. E. L. De Golyer presided, and the speakers included Dr. G. Egloff, Dr. J. B. Hill, Dr. C. K. Francis, Mr. R. Stansfield, and Mr. D. G. Smith.

Council, Officers and Committees.

Nine meetings of the Council and 38 meetings of Committees of the Council were held during the year. In addition, 16 meetings have been held of sub-Committees of the Chemical Standardization Committee.

The Council has given consideration at various times during the year to questions of professional conduct.

The following Committees of the Council have met during the year under the under-mentioned Chairmen :—

Awards Committee : *Chairman*—The President.
Benevolent Fund Committee : *Chairman*—Dr. A. E. Dunstan.
Branch Committee : *Chairman*—C. Dalley.
Chemical Standardization Committee : *Chairman*—Prof. J. S. S. Brame.
Congress Committee : *Chairman*—J. Kewley.
Election Committee : *Chairman*—J. McConnell Sanders.
Finance Committee : *Chairman*—C. Dalley.
Library Committee : *Chairman*—Prof. J. S. S. Brame.
House Committee : *Chairman*—Arthur W. Eastlake.
Publication Committee : *Chairman*—Dr. A. E. Dunstan.
Research Committee : *Chairman*—J. Kewley.

Col. S. J. M. Auld, O.B.E., M.C., D.Sc., has been re-elected President of the Institution for the year 1938–1939.

Mr. Ashley Carter, Mr. C. Dalley, Dr. F. H. Garner, Ph.D., M.Sc., Prof. A. W. Nash, M.Sc., Mr. J. McConnell Sanders, F.I.C., and Dr. F. B. Thole, D.Sc., F.I.C., have been elected Vice-Presidents for the year 1938–1939.

Mr. W. E. Gooday, A.R.S.M., D.I.C., acted as Honorary Associate Editor from January to May 1937.

Dr. F. H. Garner, Ph.D., M.Sc., was appointed Honorary Associate Editor in June 1937.

Staff.

Mr. G. Sell, who resigned his appointment as Associate Editor at the end of 1936, was the recipient of a presentation subscribed by members of the Institution.

Miss G. M. Bolton, who had been on the staff of the Institution since 1931, retired on her marriage in July 1937.

Miss B. M. H. Tripp, B.Sc., was appointed Assistant Secretary in May 1937, and has taken over much of the work connected with publications, the Library and Standardization.

The Council records its appreciation of the work of the Secretary (Mr. S. J. Astbury) and the Staff of the Institution throughout the year. It also expresses its thanks to The Rt. Hon. Lord Plender, Honorary Treasurer, Messrs. Ashurst, Morris, Crisp & Co., Solicitors, and Messrs. Price, Waterhouse & Co., Auditors to the Institution.

On behalf of the Council,
ARTHUR W. EASTLAKE,
Honorary Secretary.

INSTITUTION OF PETROLEUM

REVENUE ACCOUNT FOR THE

	£	s.	d.	£	s.	d.	*1936* £
To Administration Expenses :—							
Staff Salaries and Insurances	1417	4	6				*1612*
Honoraria	175	0	0				—
Printing and Stationery	221	1	9				*244*
General Postages	221	8	7				*215*
Telephone, Cables and Telegrams	31	11	0				*24*
				2066	5	10	
„ Establishment Charges :—							
Rent and Rates	447	18	5				*449*
Cleaning and Lighting	88	8	3				*85*
Repairs and Renewals	22	1	4				*72*
				558	8	0	
„ Publications :—							
Journal Printing	1411	5	1				*1443*
Abstractors' Fees	216	9	0				*246*
Postage on Journals	185	14	10				*198*
Cost of Other Publications	252	12	4				*211*
				2066	1	3	
„ Meetings, Hire of Hall, Preprints, Reporting, Etc.				264	17	10	*223*
„ Legal Expenses				80	0	0	—
„ Library Expenditure				46	6	7	*55*
„ Students' Scholarships				80	0	0	*80*
„ Expenses of Students' Section				30	0	7	*34*
„ Sundry Expenses				194	17	6	*159*
„ Depreciation of Office and Library Furniture and Library Books				106	18	2	*43*
„ Auditors' Fee				42	0	0	*42*
„ Grants to Branches :—							
Trinidad Branch	40	0	0				
Burma Branch	17	13	6				
Roumanian Branch	17	12	6				
Northern Branch	20	0	0				
Sundry Expenses	24	6	7				
	119	12	7				*121*
Less Transfer from Branch Fund	75	4	4				
				44	8	3	
„ Balance for the Year, Carried to Balance Sheet				719	18	1	*269*
				£6300	2	1	

RESEARCH FUND INCOME AND EXPENDITURE

	£	s.	d.	£	s.	d.
To Grants Made During Year	25	0	0			
„ Creditor	62	12	9			
				87	12	9
„ Balance as at 31st December, 1937				239	3	5
				£326	16	2

TECHNOLOGISTS.

YEAR ENDED 31ST DECEMBER, 1937.

	£ s. d.	£ s. d.	1936 £
By **Subscriptions for 1937 Received :—**			
Members...	2009 13 11		*1921*
Associate Members	1178 13 1		*1140*
Students	66 3 0		*99*
Associates	170 12 6		*168*
	3425 2 6		
Special	20 0 0		*20*
		3445 2 6	
„ **Subscriptions in Arrear, Received During Year**		145 1 11	*163*
„ **Publications**		2514 8 5	*2163*
„ **Interest and Dividends, Gross**		195 9 3	*186*
		£6300 2 1	

ACCOUNT FOR THE YEAR ENDED 31ST DECEMBER, 1937.

	£ s. d.
By **Balance as at 31st December, 1936**	316 14 5
„ **Interest Received During Year**	10 1 9
	£326 16 2

INSTITUTION OF PETROLEUM

(A Company limited by Guarantee and not

BALANCE SHEET AS

	£ s. d.	£ s. d.	£ s. d.
Capital of the Institution under Bye-Law Section 6, Paragraphs 14 and 15 :—			
Life Membership Fund—			
As at 31st December, 1936		718 10 0	
Entrance Fees—			
As at 31st December, 1936	2826 11 0		
Additions during year	192 3 0		
		3018 14 0	
Profit on Sale of Investments—			
As at 31st December, 1936		351 10 11	
Donations—			
As at 31st December, 1936		326 5 0	
			4414 19 11
Research Fund			239 3 5
T. C. J. Burgess Prize Fund			10 0 0
Members' Subscriptions Received in Advance			200 10 0
Journal Subscriptions Received in Advance			461 9 6
Sundry Creditors—General Account ...			408 18 2
Registrations Received on Account of Scottish Meeting			80 1 3
Revenue Account :—			
Balance as at 31st December, 1936 ...		1885 4 5	
Add Surplus for year as per separate Statement		719 18 1	
			2605 2 6
			£8420 4 9

Signed : S. J. M. AULD, President.
G. H. COXON, Member of Council.
S. J. ASTBURY, Secretary.

AUDITORS'

We report to the Members of THE INSTITUTION OF PETROLEUM TECHNOLOGISTS and have obtained all the information and explanations we have required. We are correct view of the state of the Institution's affairs at 31st December, 1937, accord- by the books of the Institution.

3, FREDERICK'S PLACE,
OLD JEWRY, LONDON, E.C. 2.
15th March, 1938.

TECHNOLOGISTS.

having a Share Capital.)

AT 31ST DECEMBER, 1937.

	£	s.	d.	£	s.	d.
Investments :—						
On Account of Capital—						
£461 12 0 3% Conversion Stock	491	12	6			
664 6 6 London County Council 3% Consolidated Stock	481	10	6			
806 8 3 Manchester Corporation 3% Stock 1958...	845	17	7			
867 8 6 Bristol Corporation 2¾% Redeemable Stock 1955/65	845	17	7			
150 0 0 Wandsworth District Gas Co. 5% Debenture Stock	154	8	6			
400 0 0 Metropolitan Water Board "A" Stock 1963	346	10	7			
125 0 0 Great Western Railway Co. 5% Consolidated Preference Stock	105	4	9			
150 0 0 Luton Corporation 3% Redeemable Stock 1958	151	6	7			
150 0 0 Smethwick Corporation 3% Redeemable Stock 1951/8	151	4	9			
600 0 0 Bristol Corporation 3% Redeemable Stock 1958/63	597	7	3			
				4171	0	7
(Market Value at 31st December, 1937, £3861 16*s.* 0*d.*)						
On Account of Revenue—						
£790 8*s.* 3*d.* 3% Conversion Stock	842	8	0			
On Account of Research Fund—						
£336 5*s.* 10*d.* 3% Conversion Stock	357	14	8			
				1200	2	8
(Market Value at 31st December, 1937, £1141 1*s.* 10*d.*)						
Office and Library Furniture (Excluding Presentations) :—						
As at 31st December, 1936	297	6	0			
Less: Depreciation	99	2	0			
				198	4	0
Library Books (Excluding Presentations) :—						
As at 31st December, 1936	31	4	6			
Less: Depreciation	7	16	2			
				23	8	4
Members' Subscriptions in Arrears (not valued).						
Sundry Debtors and Payments in Advance :—						
Sundry Debtors, less Reserve for Doubtful Accounts ...	272	17	2			
Payments in advance	26	4	5			
				299	1	7
Cash at Bank and in Hand				573	10	4
Cash on Deposit, General Account :—						
Chartered Bank of India, Australia and China	500	0	0			
Post Office Savings Bank	1454	17	3			
				1954	17	3
				£8420	4	9

REPORT.

that we have examined the above Balance Sheet with the books of the Institution of opinion that such Balance Sheet is properly drawn up so as to exhibit a true and ing to the best of our information and the explanations given to us and as shown

PRICE, WATERHOUSE & Co.

BENEVOLENT FUND.

Receipts and Payments Account for the Year ended 31st December, 1937.

RECEIPTS.	£ s. d.	£ s. d.	PAYMENTS.	£ s. d.	£ s. d.
Balance at Bank on Current and Deposit Accounts, 1st January, 1937 :			**Grants in Aid :**		
Benevolent Fund Account	573 16 5		Benevolent Fund	56 5 0	
Specific Endowment Fund	271 14 4		Specific Endowment Fund	100 0 0	
		845 10 9			156 5 0
Receipts during Year :			**Balance at Bank on Current and Deposit Accounts, 31st December, 1937 :**		
Benevolent Fund :			Benevolent Fund	654 5 7	
Coronation Appeal Donations	66 8 8		Specific Endowment Fund	174 13 2	
Other Donations	9 0 6				828 18 9
Subscriptions	55 1 3				
Income Tax Recovered	2 0 0				
Interest	4 3 9				
		136 14 2			
Specific Endowment Fund :					
Interest	2 12 2				
Income Tax Recovered	6 8				
		2 18 10			
		£985 3 9			£985 3 9

We have examined the above Receipts and Payments Account with the books and vouchers of the Fund and find it to be in accordance therewith. We have verified the Balances with Bankers.

3, Frederick's Place,
Old Jewry, London, E.C. 2.
15th March, 1938.

Price, Waterhouse & Co.

ANNUAL REPORTS OF BRANCHES.

ROUMANIAN BRANCH.

THE Committee have pleasure in presenting the Eleventh Annual Report for the year ending 31st December, 1937, together with accounts to this date.

Revenue Account for the Year ending 31st December, 1937.

CREDIT.		DEBIT.	
Balance on hand at December 31st, 1937 . . .	Lei 7,014	Cost of Meetings . . .	Lei 5,295
		Printing	„ 454
		Stenographer . . .	„ 3,500
		Postage, Telegrams . .	„ 1,750
Balance	Lei 7,014		Lei 10,999

The Branch Register shows the following list of Members :—

Honorary Member	1
Members	29
Associate Members	13
Student Members	2
	45

which is a decrease of three as compared with a year ago.

The Committee wish to place on record their regret at the departure of Mr. F. W. Penny, who has done as much as anybody to help the local Branch, and they wish him every success in his new undertaking.

The Tenth Annual General Meeting was held on 25th February, 1937, at which the Chairman, Mr. C. R. Young, retired and was succeeded by Mr. E. C. Masterson. It was unanimously decided that the office of Treasurer should be taken over by the Secretary. The Chairman had great pleasure in presenting the I.P.T. Student's Medal to Mr. C. Newey.

Six General Meetings were held during the year, and the Session has been one of outstanding success. The Branch had especial pleasure in receiving the visit of Dr. G. Egloff. The following were the Papers read :—

(1) *February 25th*, 1937. *55th General Meeting.*
" Engine Knock," by Mr. C. R. Young, B.Sc.

(2) *April 28th*, 1937. *56th General Meeting.*
" The Economic Operation of a Steam Drilling Rig," by Mr. D. G. Hitt, B.Sc.

(3) *May 27th*, 1937. *57th General Meeting.*
" Corrosion Problems in Petroleum Refineries," by Mr. P. Bogdan.

(4) *July 12th*, 1937. *58th General Meeting.*
" Modern Fuels and Lubricants," by Dr. G. Egloff.

(5) *October 14th*, 1937. *59th General Meeting.*
" Deep Well Pumping," by Mr. E. Boaden, B.Sc.

(6) *November 18th*, 1937. *60th General Meeting.*
" Pressure Maintenance Operations," by Mr. P. Lambright, B.S.

The Eleventh Annual Dinner was held on December 11th, 1937, under the Chairmanship of Mr. E. C. Masterson, and 89 Members and Visitors were present.

During the year Mr. L. W. Forster and Mr. G. Prikel were elected Members of the Committee of the local Branch, who are now as follows :—

Mr. E. C. Masterson, *Chairman*.
,, I. Rutherford.
,, D. I. Maxwell.
,, L. W. Forster.
,, G. Prikel.
,, O. A. Bell, *Secretary and Treasurer*.

Ex-officio Members of the Committee are :—

Mr. I. Edeleanu.
Capt. J. E. Treacy.
Mr. P. R. Clark.
,, C. R. Young.

The Committee again wish to record their thanks to the Chamber of Commerce, Ploesti, for the use of their Hall for the Meetings during the 1937 Session, and to Messrs. Brasier and Suciu for acting as Honorary Auditors.

Receipts and Payments for the Year Ending 31st December, 1937.

Receipts.

Grant from I.P.T. London by payment through Mr. O. A. Bell (see London letter of the 29th July, 1937)	Lei 14,700
Received from Dr. Suciu for 1936 subscription (authorization London letter of 26th May, 1936)	,, 1,771
Surplus 11th Annual Dinner	,, 330
Balance from 1936	,, 1,212

Expenditure.

Cost of Meetings, Printing, Postage, Lantern Slides, Chamber of Commerce	Lei 5,295	
Reports of Meetings and Stenographer	,, 3,500	
Printing (Cards for Session 1937)	,, 454	
Postages, Telegrams, Stationery	,, 1,750	
Balance on hand	,, 7,014	
	Lei 18,013	Lei 18,013

We have verified the above Receipts and Payments Account with the Books, Records, Vouchers and other Documents of the Roumanian Branch of the Institution, and having obtained all the information and explanations we have required, we are of the opinion that such account is properly drawn up to represent a true and correct statement of the Receipts and Payments for the Period under review.

C. Brasier
G. Suciu } *Honorary Auditors.*

IRANIAN BRANCH.

ANNUAL ACCOUNTS.

The Annual Accounts of the Iranian Branch for the year ended 31st December, 1937, are given below :

EXPENDITURE.

	£	s.	d.
To All Risks Insurance Premium on property		11	10
„ Cost and duty on publications	3	2	4
	£3	14	2

INCOME.

By Excess expenditure over income	£3	14	2

BALANCE SHEET AS AT 31ST DECEMBER, 1937.

	£	s.	d.		£	s.	d.
Balance as at 31.12.37 . .	19	1	1	Cash with A.I.O.C., Ltd. .	15	6	11
Less Excess expenditure over income for the year 1937 .	3	14	2				
	£15	6	11		£15	6	11

Abadan, 23rd January, 1938.

D. O. INNESS,
Hon. Treasurer.

The following have been elected members of the Committee for the Session, 1938–1939 :

Chairman : Mr. R. GORDON BROWN.
Committee : Mr. B. D. CAUTHERY.
H. DOBSON.
A. REID.
E. E. THORNELOE.
G. E. WHEELER.
Hon. Secretary : Mr. H. T. LORNE.

Mr. C. V. Rutherford is ex-officio member of the Committee at Fields.

SOUTH WALES BRANCH.

REPORT FOR SESSION 1936–1937.

A membership of nearly 90, with an average attendance of 50, indicates continued interest in the programme of lectures arranged by the South Wales Branch.

Since the last report many interesting lectures have been given covering a wide range of activities in the petroleum industry.

Among the lecturers were Dr. Egloff in June, the President himself, Colonel Auld, Dr. Dunstan, Mr. Dalley, and our own Chairman, Mr. W. C.

Mitchell, who was induced to give an extremely interesting lecture dealing with aspects of management not usually met with or realized by the rank and file.

The Secretary, as Chairman of the South Wales Section of the Institute of Chemistry, gave a lecture on the chemistry of hydro-carbons to a joint meeting with the Institute of Chemistry, so the parent body and branch membership was to that extent self-supporting.

Other lectures dealt with :—

"Cracking."
"Solvent Extraction."
"Engine Research."
"Ocean Transport."
"Bitumen."
"Lubricating Oil."

Slightly wider afield, a paper on the production of Fischer Tropsch coal spirit and its improvement by cracking by Messrs. Snodgrass and Perrin interested many outside the Branch, whilst a lecture of extreme local interest was given by Mr. E. J. Horley on "Reminiscences of Llandarcy."

Two difficulties inherent to the district will always limit extensions, *i.e.* there is only one oil refinery in the whole of Wales, and all parts of Wales are particularly badly situated for collecting a meeting from any distance more than ten miles around the centre chosen. In spite of this there is considerable keenness, and we have to regard ourselves rather as passers on of petroleum information to a fairly wide circle of people whose vocational interest in petroleum scarcely warrants their becoming members in any other than the country membership sense.

Nevertheless progress is being made quietly in extending the membership of the Parent Body where suitable applicants can be found.

E. THORNTON,
Hon. Secretary.

Llandarcy,
11th April, 1938.

NORTHERN BRANCH.

ANNUAL REPORT 1937.

The progress made since the inception of the Branch has been consolidated during the year 1937, and the Membership has been maintained and increased. There have been a few resignations due to removal from the district, but very few from other causes, and the attendance at Lectures and Meetings has also been maintained.

The General Meeting was held on 16th April. Mr. H. C. S. Fothergill was re-elected to the Chair. Mr. J. E. Haslam was elected Hon. Treasurer and Asst. Hon. Secretary, and Mr. J. E. Bennion Hon. Secretary.

During the year ten Meetings were held, the average attendance at each

NORTHERN BRANCH.

ACCOUNTS: JANUARY 1ST, 1937–DECEMBER 31ST, 1937.

RECEIPTS.	£	s.	d.	£	s.	d.
Balance . . { Bank	20	7	9			
{ Cash	1	3	10			
				21	11	7
Membership Subscriptions				42	15	0
Lecture Preprints Subscriptions				15	11	0
Annual Dinner (1937), 73 at 12s. 6d. . . .				45	12	6
Receipt from Joint Meetings				7	2	7
Sale of Books					15	0
Unused Cheques						6
Grants from Parent Institution				23	16	4
				£157	4	6

PAYMENTS.	£	s.	d.	£	s.	d.
Postage, Stationery, etc. . . .				22	15	11
Hire of Rooms for Meetings . . .				28	13	3
Dinner, March 16th, 1937	54	12	6			
Entertainers, March 16th, 1937 . .	6	6	0			
				60	18	6
Affd. Joint Chemical Societies . . .				5	13	2
Lecture Preprints				1	12	0
Sub. Petroleum Times				1	19	0
Advertising					17	6
Cheque Book					2	0
Bank Commission					4	3
	£	s.	d.			
Cash in hand	6	1	7			
„ at Bank . . .	28	7	4			
				34	8	11
				£157	4	6

(*Signed*) J. ERIC HASLAM,
Hon. Treasurer.

We have examined the accounts and certify this to be a correct Statement.
(*Signed*) E. WALPOLE.
W. COWEN.

9/3/38.

being approximately 75. The Branch has continued its association with the local scientific societies, and joint meetings have been held with the Society of Chemical Industry, the Institution of Rubber Industry, the Oil and Colour Chemists' Association, and the Institute of Fuel. The Parent Institution arranged for a Summer Meeting, to be addressed by Dr. G. Egloff, M.A., Ph.D., on the subject of "Synthesis in the Oil Industry," to which the Members of the various scientific societies in the district were invited. By the courtesy of the I.C.I. a visit of the Branch was paid to Billingham, and the party was conducted over the oil-from-coal plant and the refinery. An opportunity was also taken to see the sulphate of ammonia plant and also the power-generating plant. Some thirty-five or forty members of the branch took the opportunity of joining in this visit.

The Committee have given consideration to extending the activities of the Branch in the Liverpool district, and arrangements are being made for a meeting to be held under the auspices of the Branch in Liverpool early in the New Year, when Dr. A. E. Dunstan will give a lecture at the University of Liverpool.

The first Annual Dinner was held on March 16th, 1937, at the Midland Hotel, Manchester, under the Chairmanship of Mr. H. C. S. Fothergill, and was attended by several members of the Council, and this function proved highly successful. The Committee propose to hold a similar function annually.

The thanks of the Committee are due to the Council for clearing the deficit incurred in connection with the first Annual Dinner, and have pleasure in stating that the finances of the Branch, other than this item, are in a healthy state, there being a balance in hand which will be sufficient to meet the needs of the Branch for the 1937–1938 Session.

STUDENTS' SECTION (LONDON BRANCH).

Fourteenth Annual Report.

At December 31st, 1937, the membership of the Branch was as follows :—

Student Members . . .	38
Associated Students . .	8
	46
Awaiting election . .	9

It will be seen that the membership has shown a marked decline over the previous year, partly due to the fact that a number of students over age were removed from the register or transferred to Associate Membership. This decline is to be deprecated, as the past activity of the Branch cannot be maintained to the standards of former years without adequate and continued support. The Committee would like to take this opportunity of asking senior members to help in making the activities of the Branch known

to their junior colleagues to whom the educational value of the numerous meetings and visits cannot be too highly stressed.

The following were elected at the 14th Annual General Meeting to serve on the Committee for the session 1937–38: Messrs. Barrett, Bridgwater, Ferguson, Haworth, Hitchcock, Keach, Kirby and Wright. Messrs. Keach, Barrett and Ferguson were subsequently elected Chairman, Vice-Chairman and Hon. Secretary, respectively. During the session Messrs. Haworth and Bridgwater resigned and Mr. R. M. Stainforth was elected to fill one of the vacant places.

During the year the following thirteen meetings and four visits were arranged :—

January 20th, 1937.	Meeting. "Production," by A. Frank Dabell, M.I.Mech.E. (Member of Council).
February 4th, 1937.	Meeting. "Knock Testing," by G. M. Barrett, A.R.S.M., B.Sc. (Student).
February 18th, 1937.	Visit. Ford's Motor Works, Dagenham. Annual Dinner.
February 26th, 1937.	Annual General Meeting. "The Radioactive Factor in the Genesis and Constitution of Hydrocarbons," by E. N. Tiratsoo (Student).
March 11th, 1937.	Meeting. "The Pechelbronn Oilfields of Alsace," by A. J. Haworth, A.R.S.M., B.Sc. (Student).
March 24th, 1937.	Visit. Shell Marketing Co., Ltd., Central Laboratories, Fulham.
" "	Meeting. "High-Speed Engine Indicating in the Investigation of Fuel Quality," by J. Withers, B.Sc. (Student).
April 6th, 1937.	Meeting. "Temperature–Viscosity Relationship of Lubricating Oils," by J. H. Dove, B.Sc. (Student).
April 27th, 1937.	Meeting. "Alcohol Fuels," by A. R. Ogston (Assoc. Member).
May 8th, 1937.	Visit. National Physical Laboratories, Teddington.
May 13th, 1937.	Meeting. "Crude Oil Characteristics as Related to Geological History," by R. O. Young, B.Sc. (Student).
October 7th, 1937.	Meeting. "Some Current Chemical Problems in the Petroleum Industry," by A. E. Dunstan, D.Sc. (Past President).
October 26th, 1937.	Visit. Battersea Power Station.
November 10th, 1937.	Meeting. "Oilfield Correlations," by G. E. Higgins (Student).
November 23rd, 1937.	5th Annual Open Meeting. "Brave New Lubrication," by Lt.-Col. S. J. M. Auld, O.B.E., M.C., D.Sc. (President).
December 9th, 1937.	4th Annual Joint Meeting with I.A.E. Graduates Section, R.Ae.S. Students' Section (London Branch). "Torsional Vibrations in Engines," by R. J. W. Cousins.
December 21st, 1937.	Meeting. "Film Rupture Strength of Lubricating Oils," by N. E. F. Hitchcock, B.Sc. (Student).

The proportion of Student papers is very satisfactory, and they were all of very high standard.

Following the precedent set during the previous year, the meeting on March 24th was held in conjunction with the visit to the Fulham Laboratories through the courtesy of the Shell Marketing Co., Ltd.

Close contact with other Student and Graduate Branches in London has been maintained, and the issue of the Joint Programme has been continued. It is hoped that members of the Branch will take full advantage of the facilities available under this arrangement.

The total number attending the Branch Meetings has been maintained, although the attendance of Branch Members has, unfortunately, shown a marked decrease. This latter position is unsatisfactory, and students are asked to give more support, in order that the high standard of meetings may be kept up.

The Annual Dinner was again successful, and the Branch had the pleasure of entertaining a number of guests, including the President, Colonel Auld. The Informal Dinners held after Ordinary Meetings have been continued, although apart from the Committee very few members have attended. It is hoped that the attendance will be better in future, as it is felt that these social functions can do much to bring members together, and so consolidate the Branch.

Two entries were submitted from London for the Students Awards, and the Committee would like to congratulate Mr. E. N. Tiratsoo on being awarded a Students prize. It is hoped that there will be more entries during the coming year. The Discussion Prize was awarded to Mr. R. O. Young, who, in the opinion of the Committee, made the most valuable contributions to the discussions at meetings during the Session. Although the level of discussion has been good, it is felt that more students should take part, especially as their interest in the papers should be reflected in discussion.

The Committee would like to congratulate Mr. G. E. Higgins on winning the R.S.M. Scholarship.

The thanks of the Branch are due to the President for the interest which he is showing and the valuable suggestions he has made for the advancement of the Section, which it is hoped will bear fruit in the near future.

The Committee would also like to thank Mr. Ashley Carter for his continued interest in our activities and the valuable advice and guidance which he gives, and also other Senior Members and those of the Staff who have rendered assistance during the past year.

R. H. KEACH,
Chairman.

B. C. FERGUSON,
Hon. Secretary.

February 2nd, 1938.

THE PRODUCTION OF FISCHER–TROPSCH COAL SPIRIT AND ITS IMPROVEMENT BY CRACKING.*

By C. S. Snodgrass (Member) and M. Perrin

Synopsis.

1. Introduction.
2. Fischer–Tropsch Process.
3. Cracking of Fischer Liquid Products:
   (*a*) Selection of Plant.
   (*b*) Description of True-Vapour-Phase Process.
   (*c*) Application of True-Vapour-Phase Process.
4. Features and Scope of True Vapour Phase Process.

1. Introduction.

Recently there have appeared in the Press a number of articles regarding the synthesis of liquid hydrocarbons from water gas, notably the paper read by Prof. Martin to the Second World Petroleum Congress. Most of these papers are confined to a description and discussion of the synthetic process itself—that is, the production of liquid oil from its gaseous components. This was only to be expected, because the problem of obtaining liquid-oil products from coal is one on which there has been much expenditure and effort to find satisfactory solutions.

The two main methods are Hydrogenation and the Fischer–Tropsch Process. The first operates under conditions of high temperature and high pressure, producing motor spirit directly without the necessity of further processing. The second is a low-temperature, low-pressure process, the products from which consist only partly of motor spirit, the remainder being of a heavier character which must be converted by suitable means into motor spirit.

The production of liquid oil from coal by synthesis constitutes a fascinating subject, and the authors of the papers and articles concerned with that subject may be excused for feeling that their task has been completed when the stage of production of liquid hydrocarbons has been reached. As far as the consumer is concerned, however, that stage could scarcely be termed final, because the production of high-quality motor spirit necessitates further important processing.

2. Fischer–Tropsch Process.

It may be as well at this stage to remind you briefly of the basic principles of the Fischer Process as adopted at Holten, and in further explanation a few photographs (Figs. 5–11) are given, which indicate the extent and general layout of this installation. The raw materials are the gases carbon monoxide and hydrogen in the ratio of 1 : 2 by volume, the mixture being

* Paper read at a Meeting of the South Wales Branch held on January 14th, 1938

conveniently referred to as synthesis gas. Ordinary water-gas, as produced in a gas producer by passing steam over coke, appears to be the most economic source of raw synthesis gas. Water-gas is normally deficient in hydrogen, but this deficiency can be made up by modification in the conditions of producer operation—*e.g.* by operation at low temperature or by treating the water-gas with steam. The producers at Holten are of Humphreys and Glasgow design built in Germany, and illustrated in Fig. 5.

The crude synthesis gas, after cooling, is treated in a two-stage purification plant for the removal of sulphur. In the first stage of purification inorganic sulphur is removed according to usual gas works' practice at normal temperatures; in the second stage, organic sulphur is removed at an elevated temperature; the purification plant is shown in Fig. 6. The synthesis gas, containing hydrogen and carbon monoxide in the required proportions with less than 0·2 gm. of sulphur per 100 cu. ms., now passes to and circulates within the contact chambers (see Fig. 7). Here synthesis of hydrocarbons takes place in the gaseous phase in two stages under controlled conditions of temperature and pressure in the presence of a catalyst, which may consist of a cobalt salt distributed over a kieselguhr foundation. Under these conditions the reaction is strongly exothermic and the heat released is removed immediately by the production of steam at constant temperature and pressure.

The synthetic products from the contact chambers pass to condensing and cooling equipment (see Fig. 8), where most of the hydrocarbons and all the water formed in the synthesis are removed in the liquid state. The gas leaving the condensing equipment still contains a considerable quantity of low-boiling hydrocarbons, the greater portion of which is removed in an activated carbon plant (see Fig. 9), and is now known as charcoal (or A-K) gasoline. Two other streams are taken from the activated carbon plant, one being C_3C_4 fractions (known as gasol), and the other a lean gas consisting of CH_4, N_2, H_2, CO and CO_2. From the gasol butane and propane may be recovered (see Fig. 10), or it may be passed to the cycle-gas-system of the cracking plant for pyrolysis and polymerization.

The present practice is to divide the liquid products into two fractions, the first being charcoal gasoline of selected end-point, and the second the cracking stock. Since, in order to obtain a straight-run spirit of reasonable octane, it is necessary to cut the A-K gasoline to a low end-point, it follows that the charging stock contains a quantity of naphtha of negligible octane number. A separate yield of high-quality paraffin wax may also be obtained from the heavy condensate. Actually, the refiner who adopts the Fischer synthesis of the latest type has to consider the economic problem involved in the somewhat large production of this paraffin wax, representing about 30 per cent. of the stock which would be available for cracking. The question arises as to whether the market can absorb the straight-run paraffin wax, or whether it is desirable to crack it. This aspect also influenced selection of the cracking process, as it was found that this wax could be cracked successfully by the true-vapour-phase process, and that any wax which could not be marketed might be processed into valuable spirit.

Since the first cracking tests were carried out in 1935, the Fischer Process itself has not stood still. The introduction of increased pressure conditions in the second stage has considerably modified the quality of the liquid

products while at the same time bringing the actual yield of hydrocarbons closer to the theoretical figure. The possible theoretical yield is approximately 170 gm. per cu. m. of synthesis gas with 18 per cent. inert gases. Two years ago the attained yield stood at 100–105, but this has been successively increased, and is now stated to have reached the figure of 120–130 gm. per cu. m. It is due to the progress of these alterations and improvements in the Fischer plant that the charge to the cracking plant has varied con-

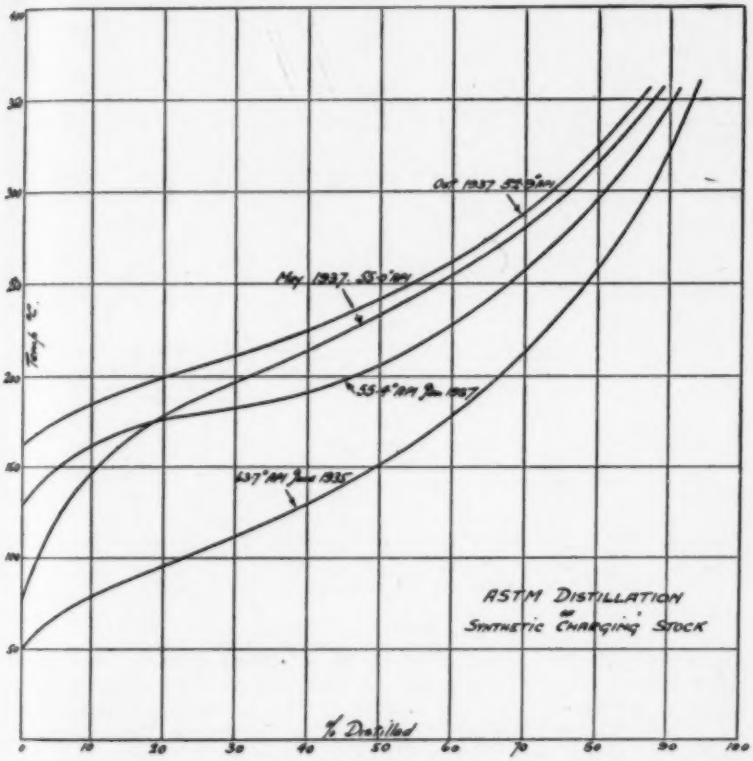


FIG. 1.

siderably since it was put into operation, and in illustration of this the graph (Fig. 1) shows the various types of Fischer crude which have been available at different times for test and commercial operation.

Table I shows some data relating to Fischer synthetic products when operating the latest system, while Fig. 11 shows a model of the complete plant illustrating clearly the various component parts. It will be seen from Table II that the increased pressure used in the second stage results in an increase of wax content, so that if higher pressures were introduced in the first stage also, a wax content of over 40 per cent. of the total liquid products would be expected.

TABLE I.

Fischer–Tropsch Process.

(January 1938.)

Particulars of Liquid Products.

Product.	Properties.				Yield % by Wt. of Total Products.		
	Boiling Range.	Sp. Gr.	Olefine Content, % by vol.		First-stage Synthesis.	Second-stage Synthesis.	Total.
			First Stage.	Second Stage.			
Wax . .	—	0·85	—	—	—	21	21
Condensate .	100–300	0·74	12	12	26·5	11	37·5
A-K gasoline .	30–150	0·66	35–40	20	26·5	8	34·5
Gasol . .	—	—	50	25–30	5	2	7
Total . .	—	—	—	—	58	42	100

Octane number of A-K gasoline { Fraction 30–140° C. . . 62 (motor method).
Fraction 30–110° C. . . 67 (motor method).

Distillation.	First-stage Product.	Second-stage Product.
I.B.P.	30° C.	30° C.
% over at 50° C. . . .	8	3
,, 100° C. . . .	29	14
,, 150° C. . . .	47	24
,, 200° C. . . .	60	35
,, 250° C. . . .	75	48
,, 300° C. . . .	85	57

3. CRACKING OF FISCHER LIQUID PRODUCTS.

(a) *Selection of Plant.*

The motor spirit of to-day is one of high anti-knock value. It so happens that, although generally the spirits distilled from coal are characterized by high anti-knock values, the Fischer–Tropsch products are substantially the reverse, and in consequence the owners of the Fischer–Tropsch process had found themselves faced with a difficult problem in converting their liquid products into high-grade modern motor spirit. It must be realized that the addition of anti-knock dopes such as tetra-ethyl lead, the use of concentrated aromatics, and the blending-in of hydrocarbon liquids produced by polymerization of gas are necessarily limited in their effects, so that the anti-knock quality of the doped or blended spirit cannot be improved by these means beyond certain limits.

Another feature of the Fischer–Tropsch oils is their highly refractory nature. The refractoriness of a cracking stock means that there is relatively little "cracking per pass," so that the oil has to be re-circulated many times through the cracking plant before cracking is completed: this calls for an excessively large plant. Alternatively, to obtain the desired degree

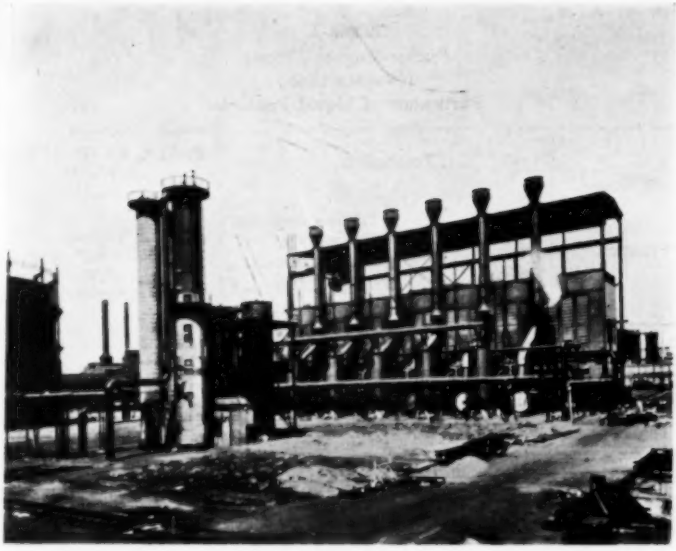


FIG. 5.
WATER GAS PLANT.

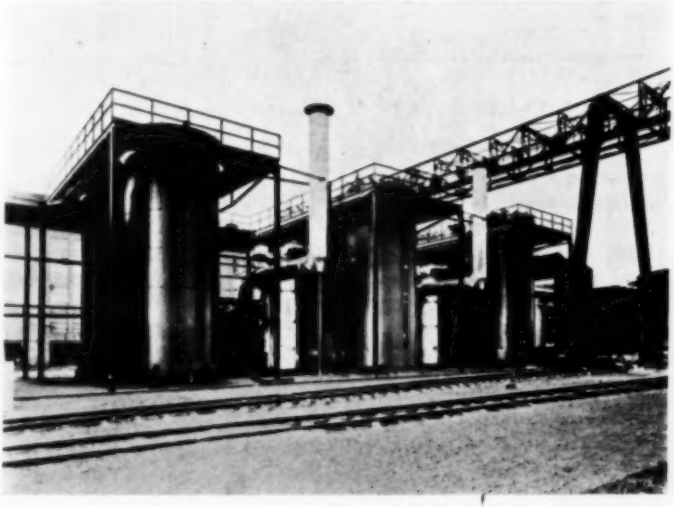


FIG. 6.
PURIFICATION TOWERS.

[*To face p.* 292.

FIG. 7.
CONTACT CHAMBERS.

FIG. 8.
GAS COOLERS FOR CONDENSATION.

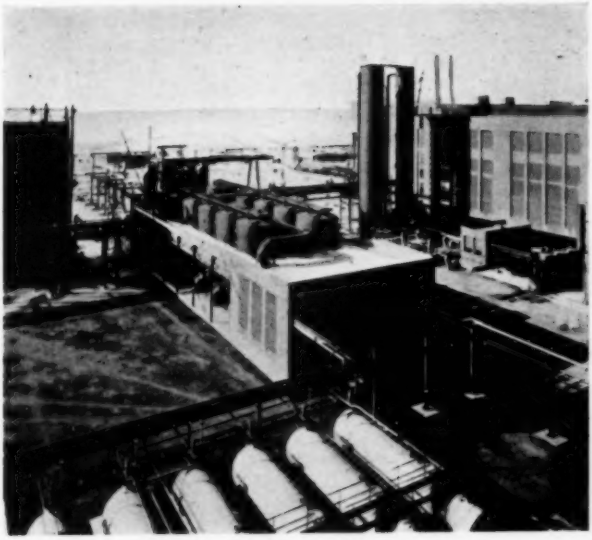


FIG. 9.
ACTIVATED CARBON PLANT.

FIG. 10.
BUTANE AND PROPANE COLUMNS.

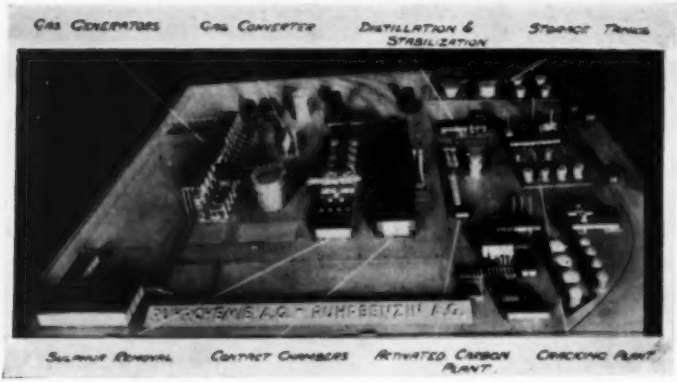


FIG. 11.

MODEL OF COMPLETE WORKS.

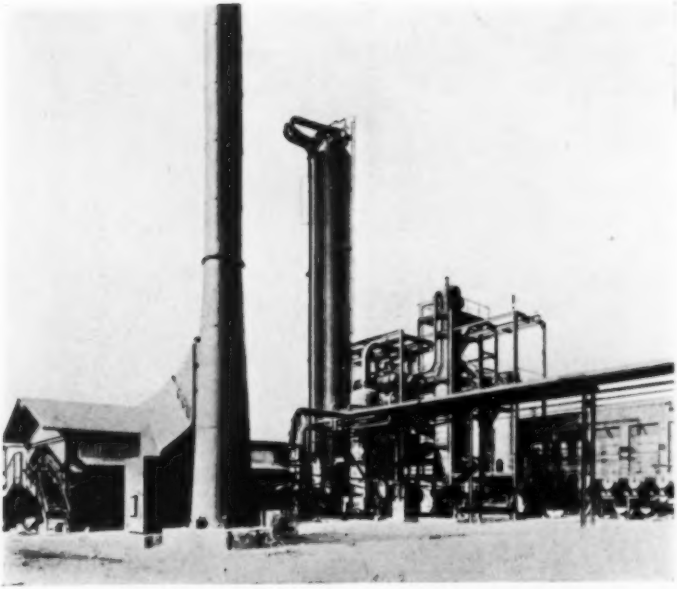


FIG. 12.

TVP PLANT IN GERMANY.

FIG. 13.
TVP PLANT IN GERMANY. FURNACE IN FOREGROUND.

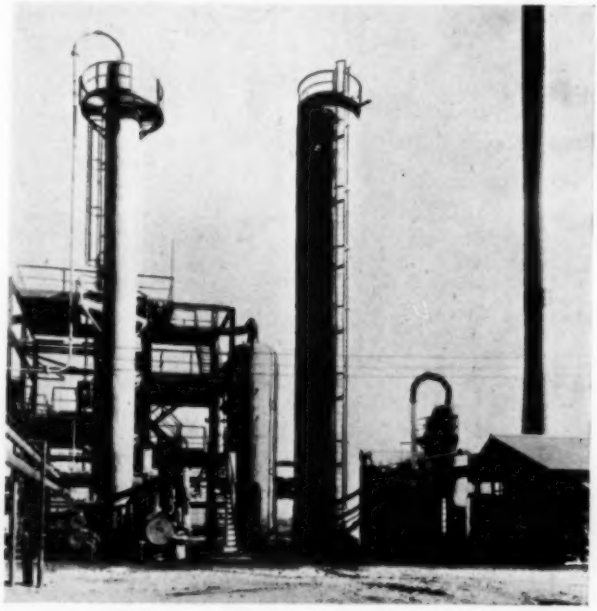


FIG. 14.
CLOSE-UP OF TVP PLANT IN THE U.S.A.

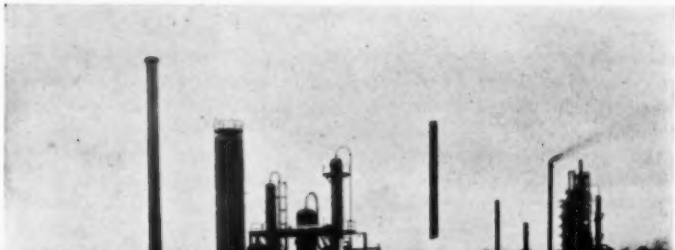


FIG. 15.
TVP PLANT IN MICHIGAN, U.S.A.

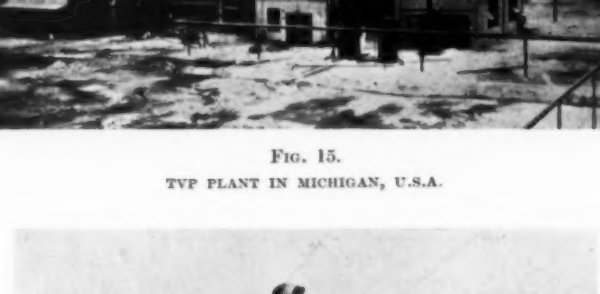


FIG. 16.
TVP CONTROL UNIT IN U.S.A.

of conversion per pass, severe cracking has to be resorted to, and this is naturally liable to bring about coking difficulties, unless the process contains features enabling the cracking reaction in the plant to be closely controlled.

In the earlier stages the Fischer–Tropsch synthetic liquid products consisted of a heavy condensate (known as Kogasin II) boiling from 100° C. to 90 per cent. over at 360° C., containing a quantity of heavy paraffin wax, and a fraction boiling with an end-point of 210° C. (known as Kogasin I), recovered from unconverted gases by activated carbon. In Kogasin I only the lighter fractions could be put to direct use, the fraction with the end-point of 145° C. having an octane number of 62 motor method : the remainder of the Kogasin I had to be further processed. Kogasin II, in the absence of further processing, could only be split into naphtha, diesel oil and solid paraffin wax by fractionation.

It was a matter of vital importance for the success of the Fischer–Tropsch Process, if it were to play its part in the German Government's programme, to find a cracking system which would convert the synthetic products into high-grade motor spirit. Furthermore, it was, of course, essential that the highest possible yields should be obtained, that conversion should take place without undue losses, that the process could be maintained in steady operation for long periods of time, and that the plant should not be of excessive size in relation to the quantity to be processed.

Exhaustive tests were carried out to ascertain which of the existing cracking processes, if any, could meet these requirements, and it was due to the exceptional features of the true-vapour-phase process that the latter was found capable of performing the task. True-vapour-phase plants were therefore specified for installation in conjunction with the first Fischer–Tropsch plants in both Germany and France. The former is at Holten near Oberhausen, and owned by Ruhrbenzin; the latter at Harnes near Lens, owned by Courrieres Kuhlmann. The reasons for this official selection by the owners of these Fischer–Tropsch plants were that, on the above-mentioned competitive tests, it was found this process gave the best yields of cracked spirit of maximum octane number, and it was clearly evident that, chiefly due to absence of coking, long uninterrupted operation of the plant could be confidently anticipated.

Furthermore, the final products from the synthesis included, in addition to the lean gas consisting of N_2, CO_2, CO, H_2 and CH_4, the so-called gasol (*i.e.* the C_3C_4 fractions). As regards this gasol, equipment was provided for recovery of propane and butane (see Fig. 10), these products having a certain sale in Germany as fuel for motor transport. However, having the ideal of maximum quantity and quality of motor spirit in mind, it was recognized that the conditions of cycle-gas circulation in the true-vapour-phase system would present the facility of converting the C_3C_4 fractions into liquid hydrocarbons, thus increasing the yield and octane number of the finished spirit. Of course, this could also have been provided for by means of a separate polymerization unit, but it was desirable to avoid additional plant if a satisfactory result could be obtained without it, and it was very doubtful if the added expense and the increased extent of plant could be justified even in Germany.

The results of these tests are summarized briefly in Table II. It should be pointed out that these results have been confirmed in commercial operation as distinct from the theoretical estimates of yield by other methods which have been quoted from time to time. Up to now (January 1938) the potentialities of producing spirits of octane numbers 70 and upwards have not been commercially exploited. The plant at Holten is at present utilized for the production of motor spirit which is not sold straight, but is blended with benzol and alcohol in accordance with German regulations. For this purpose an octane number of 63 to 64 is sufficient, but vapour pressure is maintained at a lower figure than normal—namely, at about 8 lb./in.^{2} Reid. This demand for a somewhat lower octane number is of advantage to the proprietors of the refinery, as naturally the yields are larger. It is, however, probable that the octane number will be raised in the near future to follow the tendency of the market. The figures given in Table II show that the plant is capable of following this tendency.

TABLE II.

Control Unit Test Results.

Cracking Process: True-Vapour-Phase.
Charging Stock: Fischer-Tropsch Synthetic Crude.

Charge.	Reduced Crude.			Untopped Crude.	
Sp. gr.	0·769			0·725	
Cracked spirit:					
Yield % by weight	81	75·5	65·2	70·6	65·2
Yield % by volume	88	81·8	73	72	68·3
Sp. gr.	0·7079	0·7096	0·6876	0·7114	0·6920
End-point, ° C.	200	197	168	197	160
Octane number (motor method)	62	68	75	67	73
T.E.L. required to raise octane number to 80 c.c./gal.	—	3·5	1·3	3·7	1·7

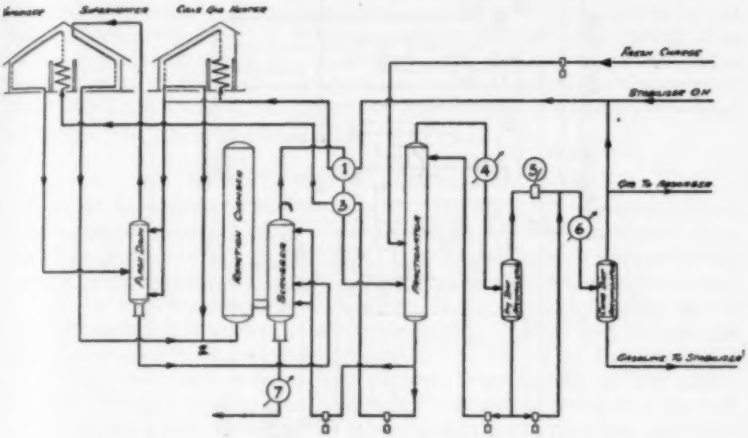
(b) *Description of True-Vapour-Phase Process.*

To understand the linkage between the Synthetic and the Cracking Processes, a description of the latter is necessary. Fig. 2 shows a simplified flow-sheet limited to the essentials of the cracking system without inclusion of the auxiliary absorption, stabilization and treating systems. The outstanding feature of the process lies in the direct heating of the oil vapours by intimate contact with a superheated inert carrier-gas, which is known as cycle-gas. This gas is a product of cracking within the system and operates in a closed cycle. For the sake of simplicity we will consider the paths of the cycle-gas and the fresh charge through the various parts of the plant separately by reference to the flow-sheet.

The cycle-gas, after heat exchange at point (1) with the overhead vapours from the scrubber, enters the cycle-gas heater, a tube still where its temperature is raised to about 650–700° C., a temperature in excess of that to be attained in the reaction chamber. At an intermediate point in the cycle-gas coil part of the gas is withdrawn and led into the flash-drum to assist

vaporization in this vessel. At point (2) the remainder of the cycle-gas meets the superheated oil vapours from the furnace, quickly raising them to the predetermined cracking temperature.

Now, considering the passage of oil through the plant, this first enters the fractionator at a point above the vapour inlet. The oil passes downward in a counter-current direction to the up-going vapours, absorbing some of their heat by direct contact, and is withdrawn with the re-cycle stock. Then, after heat exchange with scrubber overhead at point (3), it enters a conventional tube-still, known as the vaporizer, where the greater part of the charge is vaporized before entering the flash-drum. Here vaporization of the oil and drying of the vapours are completed. The stripping effect



— Simplified Flow Diagram —

— True Vapor Phase Cracking Plant —

Fig. 2.

of the flash-gas is taken advantage of for the purpose of obtaining the required vaporization without raising the temperature to the cracking range. The vapours then enter the superheater, where the temperature is raised to a point somewhat below that selected for cracking; they have now reached point (2), where we left the cycle-gas.

From here the combined cycle-gas and oil vapours are brought into intimate contact with each other, and enter the reaction chamber together, where the excess heat of the former instantly raises the temperature of the latter to the cracking point. The size of the reaction chamber and the quantity of the cycle-gas are so adjusted as to effect just the desired amount of cracking. Furthermore, this constitutes a means of controlling not only the extent of the cracking to be done, but also the way in which the cracking is to proceed. The cracked products and cycle-gas from the reaction chamber enter the lower part of the scrubber through a transfer line. In

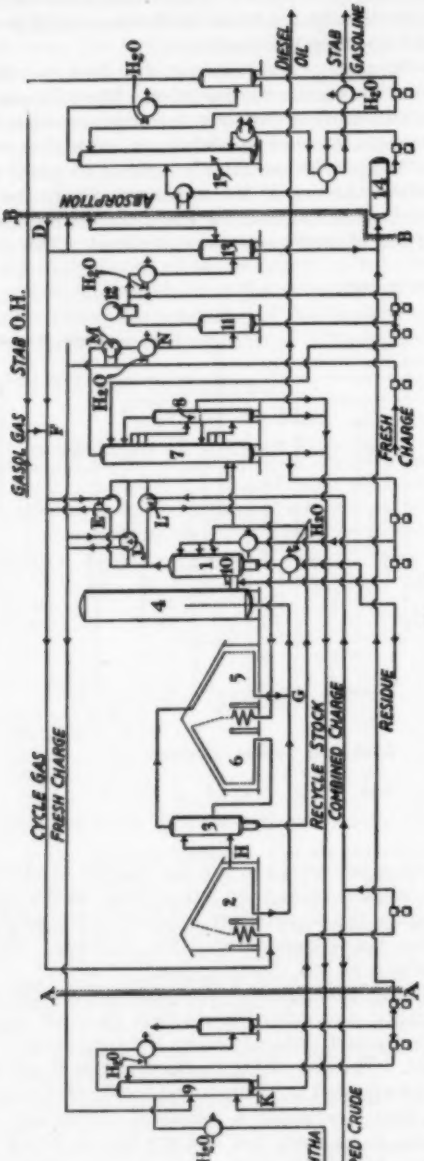


FIG. 3.

COMBINATION PLANT FOR PROCESSING SYNTHETIC OIL.

the scrubber the vapours and gas are cooled, fuel oil is blown down via cooler or exchanger (7), and the remaining gases and vapours are taken overhead to the fractionator, being subject to further cooling at points (1) and (3) as above mentioned.

The overhead vapours from the fractionator pass through condenser (4) to a heavy distillate accumulator, the overhead gas and vapours from which pass, *via* compressor (5) and condenser (6), to a combined distillate accumulator. The heavy distillate from the first accumulator, which also provides the fractionator reflux, is pumped into the discharge line from the compressor and, acting as an absorption medium, passes, together with the gas and light distillate, into the second accumulator. Excess gas leaving this accumulator is led off to the absorber, and the remainder returned to the plant as cycle-gas, the cracked spirit being taken to the stabilization plant. Fig. 3 indicates diagrammatically the layout of a cracking plant operating in conjunction with Fischer Synthesis. This shows topping of the combined synthetic liquid products, stabilization of the cracked and straight-run spirits, and introduction of stabilizer overhead and gasol into the cycle-gas system.

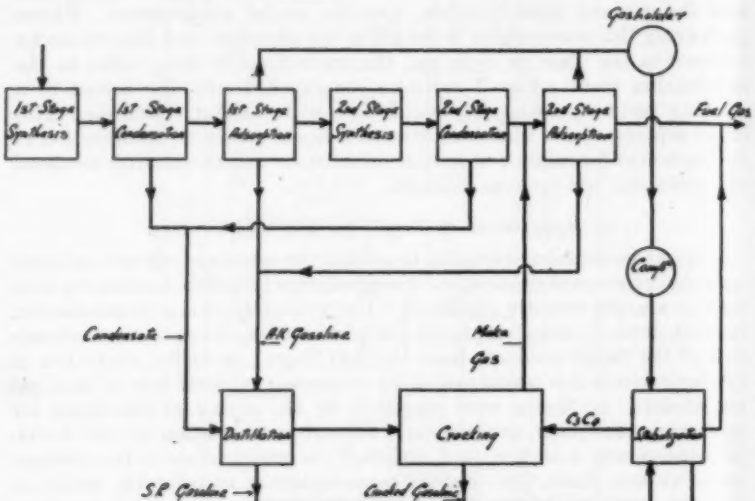
(c) *Application of True-Vapour-Phase Process.*

It might be considered feasible to submit the synthetic vapours to direct cracking before condensation, and a suggestion to this effect has already been made in a paper recently published. Unfortunately, this is impracticable, because, firstly, synthesis is carried out in two stages, necessitating condensation of the liquid products from the first stage; secondly, every ton of synthetic product is accompanied by thousands of cubic feet of lean gas and steam: no means were suggested by the author of this paper for separating the gases and vapours without condensation of the latter. In consequence, it is clear that, although the products are in fact cracked in the vapour phase, intermediate condensation is unavoidable, and it is, therefore, not possible to make use of the large saving which might be effected if this step could be avoided. Fig. 4 shows diagrammatically how the various parts of the Fischer true-vapour-phase plants are linked together. Charging of stabilizer overhead and gasol into the cycle-gas system has not yet been carried out in practice sufficiently long to enable the increase in yield and octane of the spirit to be tabulated. These naturally depend on the quantity of the gasol available.

In the application of this cracking system to the Fischer–Tropsch products, certain specific problems had to be solved; as an example, the amount of charging stock available per day called for a cracking plant which was comparatively small. For this reason the various coils were small, and it was found advisable to combine them all into one heater. This necessitated very careful design, in order to evolve a heater in which the outlet temperatures of several coils could be controlled. Further, in most cracking plants the cracked gas is utilized for the firing of the heater, but in the Fischer–Tropsch installations the cracked gas is taken into the main gas system. The gas used for firing the cracking-plant heater is the waste gas from the Fischer plant, which has a low calorific value of normally about 300 B.T.U. per cu. ft. or less, and this calorific value is subject to considerable fluctuations. The low calorific value of the gas

calls for special design of burners, and the fluctuations in its calorific value necessitate special control equipment. However, these problems have been satisfactorily solved and steady operation has been obtained.

Another feature is the limited amount of residue produced. This varies between 2 and 4 per cent., according to the nature of the charging stock. The withdrawal of such a small quantity of residue from the plant cannot be carried out if uniform quality of residue is to be retained, and a residue stripper has therefore been installed, enabling any excess quantity of residue to be withdrawn from the scrubber. The quality of the fuel oil is controlled



COMBINED FLOWSHEET
FISCHER - TVP

FIG. 4.

in the stripper. The recycle carried with the residue goes overhead from the stripper, is condensed, and then pumped back into the main plant.

The treatment of the raw spirit is of a simple character. Both the cracked gasoline and the straight-run spirit are passed through clay towers. The treating loss here is in the range of 5 per cent. but the bulk of this loss consists of polymers which are returned to the cracking plant together with the cracking stock, leaving a nett treating loss of 1–2 per cent. Subsequent to clay treating the gasoline is subjected to soda wash. The colour is 25 Saybolt or higher.

Figs. 12 and 13 show views of the cracking plant, constructed by Messrs. Gütehoffnungshutte, while Fig. 11 is a bird's-eye view in model form of the entire Fischer plant and auxiliary equipment. The following is a summary of results obtained by cracking the heavier fractions of Fischer crude in

the true vapour phase and blending with A-K Gasoline from the activated carbon plant.

TABLE III.

True-Vapour-Phase Cracking of Fischer–Tropsch Synthetic Liquid Products.

Yield of 195° C. End-point Spirit by Topping, Cracking, and Blending.			
Octane number (motor method) of finished blended spirit	63	68	70
Yield % by weight of total liquid products.			
Cracking stock	57·5	60	70
A-K gasoline (unstabilized)	42·5	40	30
Total stock	100	100	100
Cracked spirit (stabilized)	44	44·5	47
A-K gasoline (stabilized)	40	37·5	28
Total blend	84	82	75

4. FEATURES AND SCOPE OF TRUE-VAPOUR-PHASE PROCESS.

A point of fundamental importance is that the quality of a motor spirit produced from a given stock by cracking depends mainly on the character of the cracking reaction employed; the tendency of present-day cracking is in the direction of increased temperatures. This tendency is responsible for bringing vapour-phase cracking to the forefront Some years ago the high temperatures required with vapour-phase cracking were regarded as constituting an objection to this type of operation. At that time the progress of metallurgy had not reached the point at which it stands to-day, and the high temperatures involved could not then be attained with the safety and dependability which present-day materials can offer to the refiner.

All true-vapour-phase plants, whether for petroleum or synthetic oils, embody re-circulation of the heat-carrier medium. With this specific feature almost any desired degree of vaporization is obtainable in the flash-drum without unduly raising the vaporizer-outlet temperature. By admitting high-temperature cycle-gas into the reaction chamber, the superheater outlet temperature can be adjusted to the optimum quality of the final product. Regulation of the quantity and temperature of the cycle-gas makes it possible to control the temperature gradient and the cracking reaction: this signifies control of the initial temperature of the reaction and of the rate at which the temperature falls until the reaction is completed and the hydrocarbons quenched to remove them from the cracking range at the desired moment. By this means plant conditions can be readily adjusted to suit different types of charging stock and the required specifications of the finished products.

It is well known, of course, that the time-temperature curve of the cracking reaction affects the quality of the product to a very great extent, and that, to obtain the optimum quality, it is very essential to be in a position to control the speed of the heating and of the cooling of the hydrocarbons. It is for this reason that, with this method of cracking, optimum results are obtainable. The rise of temperature in the hydrocarbons from the range

of slow cracking to the point of intensive cracking can be brought about with the desired speed, and the fall of temperature in the reaction chamber can be controlled by the medium of the mass effect of the inert gas present.

Absence of coke formation, both in the tubes of the heaters and the reaction chamber, is a point of outstanding importance. In the former case this is due to the fact that cracking of the vapours is performed in the reaction chamber, and the temperature in the coils is one at which little or no cracking takes place; in the latter it is due to the effect of the cycle-gas in retarding the intermediate condensation between production of aromatics and the formation of coke. This appears to be supported by the fact that true-vapour-phase motor spirits have exceptionally high aromatic contents. Furthermore, the absence of coke formation renders this system applicable to any stock, the refractoriness of which may cause difficulties if cracking were attempted in any other manner.

Another valuable feature of the true-vapour-phase principle is that the hot cycle-gas can be made use of in a non-residuum operation for injection into the coke chambers, whereby the volatile content of the coke is greatly reduced and its value correspondingly increased.

The conventional cracking plant of to-day may only be complete when a reforming plant and a polymerization plant are added, both for the purpose of improving the octane number of the products. A true-vapour-phase plant is, however, complete without this additional equipment, because the basic principle of the system is such as enables these functions to be performed within the plant itself. The preheating of the cycle-gas in the furnace to temperatures at which polymerization of unsaturates into liquid gasoline of high octane number takes place raises the quality and increases the quantity of the yield without any additional equipment.

TABLE IV.

Typical Results of True-Vapour-Phase Cracking.

Type of Charging Stock.	Reduced Crude.	Heavy Gas Oil.	Naphtha.	Shale Oil.
Source	Iraq	Barbers Hill	Bradford	Tasmania
Sp. gr.	0·903	0·889	0·727	0·909
Yields % by volume:				
Motor spirit	46	60	81	50
Fuel oil	44	26	2	41
Gas and loss	10	14	17	9
	100	100	100	100
Properties of stabilized spirit:				
Sp. gr.	0·756	0·788	0·793	0·817
End-point, ° C.	211	214	210	220
Octane number (motor method)	72	78	73	75
Blending value (motor method)	83	87	80	88
Vapour pressure (Reid), lb./in.^{2}	9·0	10·0	6·0	4·4
Fuel oil:				
Sp. gr.	1·038	1·05	1·05	1·07

These special features of the true-vapour-phase cracking process serve when they are applied to the cracking of various types of charging stock, to produce motor spirit of better anti-knock value than is obtainable by conventional methods of cracking. Typical results are shown in Table IV.

Figs. 14 and 15 are typical of true-vapour-phase plants operating on a heavy reduced petroleum crude in the U.S.A. Fig. 16 illustrates the control unit where complete facilities are available for testing all varieties of charging stocks.

The difficulties which retarded the early progress of true-vapour-phase cracking, especially the metallurgical questions involved in the use of high temperatures, referred to above under the heading of "Features and Scope of True-Vapour-Phase Process" have now disappeared. No difficulty is experienced in installing equipment designed for heating cycle-gas to temperatures of 650–700° C. While, in common with every other process, much development work remains to be done, recognition has been given to the advantages of the process, particularly in respect to the high anti-knock qualities of the cracked spirit which it can produce. Apart from Fischer–Tropsch synthetic oils, the successful application of the true-vapour-phase process to all varieties of charging stocks from shale oils and the heaviest reduced crudes to light naphthas has been abundantly proved.

The authors would like to acknowledge the kind assistance of Messrs. Ruhrchemie A.G. for the supply of data and photograghs, Messrs. Gütehoffunngshutte A.G. for the supply of photographs and the Editor of the "Industrial Chemist" for the loan of the block of Fig. 3.

ERRATA.

"The Correlation of Tests on the Ignition Quality of Diesel Fuels, carried out at Delft and Sunbury," *Journal*, July 1936, p. 460.

Column 1, *line* 22 *et seq.* *For* Acetyl Peroxide *read* Acetone Peroxide.

Column 1, *line* 28. *For* M + 1% Acetyl Peroxide *read* M + 1·6% Acetone Peroxide

SATURATED HIGH OCTANE FUELS WITHOUT HYDROGENATION. THE ADDITION OF OLEFINES TO *ISO*PARAFFINS IN THE PRESENCE OF SULPHURIC ACID.*

By S. F. Birch, A. E. Dunstan, F. A. Fidler, F. B. Pim and T. Tait.

(Research Dept., Anglo-Iranian Oil Co., Ltd., Sunbury-on-Thames, Middlesex.)

In the last few years the notable situation has developed in which the engine designer has been outpaced by the chemist—that is to say, fuels have become available which are too good for the most extreme requirements of current types of engines. This state of affairs is, however, unlikely to be of long duration, and there seems little doubt that in the near future the demand for such fuels will even exceed the supply.

Of the materials suggested as basic fuels for high octane blends the most satisfactory are certain *iso*paraffinic hydrocarbons and di*iso*propyl ether. The latter, while possessing excellent blending characteristics and lead susceptibility, suffers from the disadvantage of having, in common with other oxygen-containing fuels, a somewhat lower calorific value than a hydrocarbon fuel. Whether this need be seriously considered for most practical purposes is doubtful, although, as Barnard points out (*Nat. Pet. News*, 3.31.37, 65), a time may well come when the exclusive use of high-octane fuels will be justified economically by making possible very low cruising fuel consumption. This would, of course, tend to penalize low-calorific-value fuels.

Even though rated in the 100 + octane range, aromatic hydrocarbons are not regarded at present as satisfactory aircraft fuels on account of their temperature sensitivity, although a reversion to water cooling, which Heron regards as not altogether improbable, would bring them into a position of very considerable importance.

The advantages offered by the *iso*paraffinic type of fuel for use in aircraft engines of high power output have resulted in a considerable amount of research directed towards producing suitably highly rated *iso*paraffins in reasonable quantities and at reasonable cost. Of these the production of *iso*-octane (2 : 2 : 4-trimethylpentane) and an isomeric *iso*-octane obtained by the hydrogenation of the butene-*iso*butene condensation product has been satisfactorily worked out, and several plants for their production have been erected or are in course of erection. The production of a third *iso*paraffin—*iso*pentane—by straight fractionation for use in place of the low-boiling fractions to provide volatility, has also materially aided in the production of high-octane fuels. The use of *iso*pentane, is, of course, restricted owing to its low boiling point, so that it cannot be regarded in the same category as *iso*-octane.

* Paper received May 2nd, 1938.

Since both *iso*-octanes are derived from *iso*butene, the amount of the latter hydrocarbon available must eventually determine the *iso*-octane production. The more recently discovered process in which, as a preliminary step, *iso*butene and butene are condensed has the advantage over the older method, involving only *iso*butene, of doubling the yield. Admittedly the octane rating of the product obtained by the former process is somewhat lower—95 against 99–100 O.N. for commercial *iso*-octane—but the greatly enhanced yield more than compensates for this. Both processes involve hydrogenation, with its attendant disadvantages and comparatively high costs.

Theoretically, the combination of *iso*butene with *iso*butane should give *iso*-octane, a possibility which occurred to Parks and Todd (*Ind. Eng. Chem.*, 1936, **28**, 418–419). Such a reaction, they concluded from thermodynamical considerations, would be possible, although the relatively low temperature necessary, coupled with the chemical inertness and low reaction velocities usually attributed to paraffin hydrocarbons, made the feasibility appear dubious. In fact, they did not publish their results until after Ipatiev and v. Grosse (*J. Amer. Chem. Soc.*, 1935, **57**, 1616) had succeeded in carrying out the reaction, using as catalyst boron trifluoride activated with nickel powder, and either water or hydrogen fluoride. From the wide boiling range of the product given by Ipatiev and v. Grosse, it is obvious that the reaction is by no means limited to simple combination of the olefine with the *iso*paraffin. At a later date Ipatiev and Komarewsky (*J. Amer. Chem. Soc.*, 1936, **58**, 913) succeeded in effecting the combination of olefines with paraffins in presence of aluminium chloride. Reaction was not limited to *iso*paraffins, and normal paraffins were found to react, although, since aluminium halides have been shown by Glazebrook, Phillips and Lovell (*J. Amer. Chem. Soc.*, 1936, **58**, 1944) and more recently by Montgomery, McAsteer and Franke (*J. Amer. Chem. Soc.*, 1937, **59**, 1768) to be capable of isomerizing normal to *iso*paraffins, there seems little doubt that isomerization is an essential preliminary.

The addition of olefines to paraffins has also been effected non-catalytically by Frey and Hepp (*Ind. Eng. Chem.*, 1936, **28**, 1439) by employing high temperatures and pressures (510° C. and 300 atm., respectively) and using a large excess of paraffin. The formation of the hydrocarbons to be expected by straightforward addition was demonstrated, but the yields were low.

The production of *iso*-octane by the direct combination of *iso*butene with *iso*butane is a particularly attractive problem for investigation. Not only would such a reaction increase the potential supply of *iso*-octane, but it would also eliminate hydrogenation and at the same time find a use for *iso*butane, a hydrocarbon having at the present time little more than fuel value. The ease with which it has been found possible to carry out this reaction and obtain excellent yields under surprisingly mild conditions still remains a source of astonishment to the authors. Thus *iso*butene and *iso*butane react readily at ordinary temperatures in the presence of sulphuric acid (97 per cent.) to give a product consisting essentially of *iso*paraffins of high octane rating and containing, particularly under certain conditions of operation, a high proportion of *iso*-octanes.

Although several theories have been advanced to explain the mechanism

of olefine polymerization, none can really be considered entirely satisfactory, probably because more than one type of reaction is involved. Undoubtedly secondary reactions, in particular those involving isomerization, obscure the issue by making it difficult to distinguish the primary reaction products. This is particularly true of reactions involving acid polymerization, especially those using phosphoric acid, which necessitate operating under comparatively drastic conditions of temperature and pressure. Whatever the mechanism of polymerization, the first step appears to be the formation of an active molecule, fragment or ion possessing extremely reactive properties. It can, for example, react with a second olefine molecule either similar to that from which it was itself derived to form a true polymer or with a dissimilar olefine molecule to give a condensation product (poly-condensation). Similarly, reaction can take place with alcohols to give ethers and with aromatic hydrocarbons to form the corresponding alkyl derivatives. The active group or molecule is thus able to react with hydrogen atoms in certain molecules or configurations with considerable ease. The addition of olefines to aromatic hydrocarbons is of especial interest owing to the resemblance in the behaviour of hydrogen atoms attached to the aromatic nucleus and those attached to the tertiary carbon atom of *iso*paraffins.

The inertness usually attributed to paraffins has, particularly in recent years, been shown to be much less marked than had been formerly supposed. Furthermore, it has become increasingly obvious that *iso*paraffins are far more reactive than the corresponding normal members, the increased activity centring round the tertiary carbon atom. Like the hydrogen atom of the aromatic nucleus, this is readily attacked by such reagents as chlorsulphonic and nitric acids, reacts readily with acid chlorides in the presence of aluminium chloride and may be replaced by chlorine under very mild conditions (cf. Schaarschmidt, *Petroleum*, 1932, **28**, No. 12, 1–4).

The reaction of olefines with aromatic hydrocarbons, first observed by Brochet (*Compt. rend.*, 1893, **117**, 115), has been investigated by a number of workers. More recently Ipatiev and his collaborators (*J. Amer. Chem. Soc.*, 1936, **58**, 919) have shown that the reaction can be carried out by adding the olefine to an agitated and well-cooled mixture of the aromatic hydrocarbon and concentrated sulphuric acid to give a good yield of the corresponding alkylated hydrocarbons. It was later shown (*J. Amer. Chem. Soc.*, 1936, **58**, 1056) that di*iso*butene under similar conditions behaved abnormally, reacting as though depolymerized and giving *tert.*-butyl derivatives.

The possibility of extending this type of reaction to olefines and *iso*paraffins therefore appeared to be the obvious line of attack, and an attempt was made to condense di*iso*butene with *iso*butane under conditions similar to those employed by Ipatiev and Pines. The reaction was found to proceed smoothly and to give a good yield of a product having a low gravity and bromine number, but boiling over a wide range. After removal of unchanged *iso*butane by distillation, a fraction was obtained boiling in the gasoline range between 27° and 185° C. This was water-white, fully saturated, and constituted the main bulk of the product. From its low gravity and high octane rating (approximately 90 O.N. C.F.R. Motor Method), it obviously consisted largely, if not entirely, of *iso*paraffins. The

residue, pale yellow in colour, also apparently consisted substantially of *iso*paraffins, together with some olefinic hydrocarbons. The octane number of this material, about 85 O.N., confirmed its high *iso*paraffin content.

Further investigation showed that the reaction was general in character and could be applied to a variety of *iso*paraffins and olefines. Of the former so far examined, *iso*butane, *iso*pentane and *iso*hexane (2-methylpentane) were found to react readily, although *iso*-octane (2 : 2 : 4-trimethylpentane) failed to do so.* The olefines investigated included propylene, butene-1, butene-2, *iso*butene and its di- and tri-merides, trimethylethylene and the butene–*iso*butene addition product (B.I.B.), all of which reacted smoothly and gave good yields of saturated products boiling in the gasoline range.

As was to be anticipated, no combination apparently occurred when *n*-butane was substituted for *iso*butane in the reaction with di*iso*butene, the product being that ordinarily obtained when the latter is treated alone with acid under similar conditions.

Not all olefines appear to react with equal facility, the ease with which polymerization takes place under the conditions of the reaction being an important factor in determining the extent to which the *iso*paraffin addition occurs. Thus, an olefine which is easily polymerized by concentrated acid will react smoothly with an *iso*paraffin under similar conditions. For example, *iso*butene and trimethylethylene are polymerized vigorously at 20° C. by 97 per cent. acid and both combine readily with *iso*butane under these conditions. Propylene is not so easily polymerized and a slightly higher acid concentration is desirable to obtain satisfactory results.

The fact that certain olefines may be used in their polymerized form, and yet react as though depolymerized to the corresponding monomers, is of considerable interest and importance. How far this is generally applicable is as yet unknown. Both di- and tri-*iso*butenes behave in this way, as does also the butene–*iso*butene addition product (B.I.B. or Selecto Polymer), which reacts as though it were an equivalent mixture of butene and *iso*butene. Furthermore, since an 80–120° C. cut from polymer gasoline gave a product similar to that obtained from the C_3 and C_4 olefines, from which it had been derived, it appears probable that this type of polymer also undergoes depolymerization or scission in the same way. The breaking of the polymer molecule where union originally took place shows a definite weakness at this point which, at least in the C_8 series, persists even after hydrogenation. Thus, both *iso*-octane (2 : 2 : 4-trimethylpentane) and the hydrogenated butene–*iso*butene addition product (largely 2 : 2 : 3-trimethylpentane) are broken down by prolonged stirring with 97 per cent. acid at ordinary temperatures to give, along with other hydrocarbons (cf. Brooks, Cleaton and Carter, *J. Res. N.B.S.*, 1937, **19**, 319–333), *iso*butane and a mixture of *iso*- and *n*-butane, respectively (Fig. 1).

The procedure involved in carrying out the reaction is simple and does not necessitate the use of high temperatures or pressures, the following

* An attempt was made to induce methyl*cyclo*hexane, which also possesses a hydrogen atom attached to a tertiary carbon atom, to react, but failed possibly owing to some steric effect.

description of the method adopted for the di*iso*butene–*iso*butane reaction being typical.

Sulphuric acid (97 per cent.) and *iso*butane are placed in a vessel, capable of withstanding low pressures, fitted with an efficient stirrer and jacketed so that it can be maintained at any desired temperature by the circulation of hot or cold kerosene, and the olefine run in during vigorous agitation over a period of 90 minutes. The temperature is maintained at 20° C. by

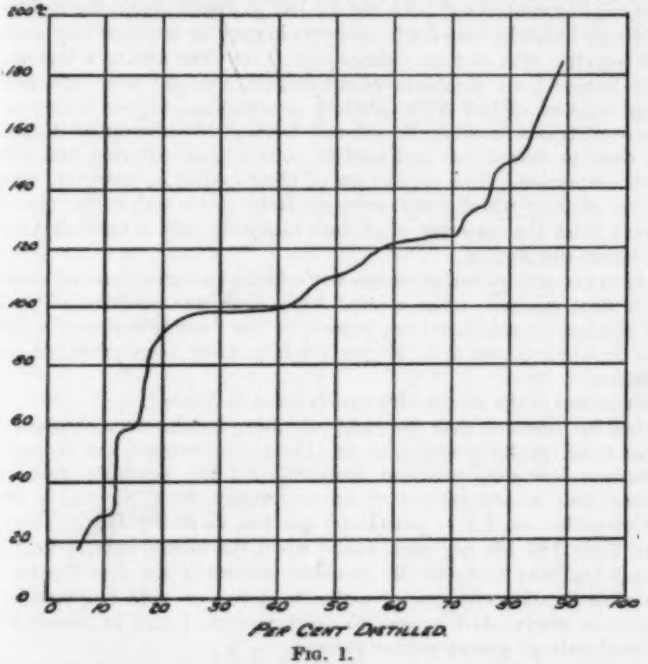


FIG. 1.

DISTILLATION CURVE (25-PLATE COLUMN) OF LIQUID PRODUCT FROM ACTION OF 97 PER CENT. SULPHURIC ACID ON *iso*-OCTANE AT NORMAL TEMPERATURE.

the circulation of cold kerosene, which removes heat liberated in the reaction. During the time the pressure falls from 45 to 50 lb./sq. in. (gauge) to atmospheric. When addition is complete, agitation is continued for a further 30 minutes, after which the reaction product is cooled down to facilitate working up. This entails removing the acid—usually pale brown in colour, darkening rapidly on contact with air—and neutralizing the hydrocarbon layer with a caustic soda wash. Since the product always contains unchanged *iso*butane, this is recovered by distillation. The residual *iso*butane-free product is water-white in colour, possesses a pleasant odour characteristic of *iso*paraffins, a bromine number (Francis) of 2–5 and a specific gravity of 0·700–0·715/15·6° C. The distillation is continued until the column-head temperature reaches 185° C. The residue, which represents about 15 per cent. of the yield, is usually pale yellow to brown

in colour, has a bromine number (Francis) of approximately 14 and a gravity of 0·783/15·6° C.

The fraction boiling up to 185° C. has a pleasant sweet odour and is entirely saturated. It has specific gravity 0·705/15·6° C. and an octane rating of 90 O.N. (C.F.R. Motor Method) rising to 100 O.N. on the addition of 1·5 c.c. T.E.L. per (Imp.) gal. The yield of this fraction is generally 140 per cent. based on the olefine taken.*

The sulphur contents of both the 27–185° C. fraction and the residue are exceedingly low, which no doubt accounts in part for the good lead response. When working with certain olefines—*e.g.*, propylene and to a less marked extent butene-1—if complete neutralization has not been effected, the sulphur content of the crude product is somewhat higher, owing to the presence of traces of sulphuric esters. During the subsequent distillation these tend to decompose and lead to considerable charring and sulphur dioxide formation. The production of these bodies is, however, confined to those olefines which form comparatively stable sulphates, the crude products from the majority of olefines requiring only a very slight alkali wash before distillation.

Only in exceptional instances has any refining treatment proved necessary for the final product, when a small soda wash was effective—*i.e.*, either when sulphur dioxide has been formed by the decomposition of sulphuric esters or when traces of hydrogen sulphide have been produced during distillation.

A summary of the results obtained is given in Table I.

It will be observed that the most promising results were obtained from the reactions involving *iso*butane and the poly*iso*butenes, the butenes and the butene–*iso*butene addition product. All the products from these reactions had octane ratings of approximately 90 O.N., which on the addition of 1·5 c.c. T.E.L. per (Imp.) gal. rose to 98–100 O.N. The yields varied from 146–164 per cent. based upon the olefine taken—*i.e.*, 73–82 per cent. of that theoretically possible, assuming the combination of 1 mol. of *iso*paraffin with one of a simple olefine or, with polymerides and addition products which appear to depolymerize, 1 mol. of *iso*paraffin for each molecule of parent olefine formed.

The *iso*Butane–*iso*Butene Reaction.

Since the reaction of *iso*butane with *iso*butene and its polymers was found to give identical products, the latter have been employed for most of the experiments carried out on this reaction. Owing to the promising nature of the results and the value of the products obtained, the effect of variation in the reaction conditions has been studied in some detail.

Of the conditions affecting the reaction, the temperature, the ratio of the reactants and the acid concentration appear to be the most important.

The optimum reaction temperature when using 97 per cent. acid lies in the region of 20° C. At higher temperatures there is a considerable amount of oxidation with formation of sulphur dioxide and fouling of the acid;

* For convenience, yields are based upon the weight of olefine taken. The theoretical yield for the di*iso*butene–*iso*butane reaction is thus 204 per cent.

Table I.

Summary of Runs Carried Out in Lead-lined Autoclave with Equimolecular Ratios of Paraffin and Olefine and at a Temperature of 20° C.

TABLE I.

Summary of Runs Carried Out in Lead-lined Autoclave with Equimolecular Ratios of Paraffin and Olefine and at a Temperature of 20° C. Time of addition 90 minutes. Time of agitation 30 minutes.

Run No.	Reactants.		Concn. of H_2SO_4, %.	Yield % of Material >27° C. on Olefine Taken.	Product 27–185° C.					Residue.		
					On Olefine Taken, %.	Sp. gr. at 15·6° C.	Bromine Number (Francis).	Octane Rating.		On Olefine Taken, %.	Sp. gr. at 15·6° C.	Bromine Number (Francis).
	Paraffin.	Olefine.						Neat.	+1·5 c.c. T.E.L./(Imp.) gal.			
42A	*iso*Butane	Di*iso*butene	96·9	165	136	0·705	<1	90·5	98	22	0·783	14
30 | 49 /	*iso*Butane	Tri*iso*-butene	96·9	163	138	0·704	<1	88·7	98·9	20·5	0·782	3·5
63	*iso*Butane	B.I.B. (105·5–112° C.)	97	158	135	0·707	<1	87·0	97·9	20	0·784	15
71	*iso*Butane	B.I.B. (95–120° C.)	97	164	137	0·703	<1	89·4	99·5	22·9	0·7815	14
26	*iso*Butane	Polymer gasoline (80–120° C.)	97	—	—	—	—	84·6	95·5 (+2 c.c.)	—	—	—
40	*iso*Butane	Propylene *	100·6	150	122	0·698	<1	82·5	93·3	23	0·774	2·5
62	*iso*Butane	Butene-2	97	164	148	0·706	<1	90·2	100·3	14·8	0·785	10
97	*iso*Butane	Butene-1	97	159	139	0·708	2	89·1	98·1 ‡	20·5	—	—
73	*iso*Butane	Trimethyl-ethylene	97	152	121·5	0·706	1	86·1	98·5	26·5	0·786	19
77	*iso*Pentane	Di*iso*-butene †	97	159	120	0·712	<1	79·7	90·4	38·4	0·787	23
56	*iso*Hexane (2-methyl-pentane)	Di*iso*butene	97	217 (after removal of unchanged *iso*paraffin)	159·5	0·6955	<1	77·6	—	54·3	0·785	20

* Temperature 30° C.
† The product was cut at 40° instead of 27° in order to remove *n*-pentane, originally present as impurity in *iso*pentane.
‡ 1·0 c.c. T.E.L./(Imp.) gal.

TABLE II.

Effect of Varying Ratio of Reactants.

Diisobutene and isobutane at 20° C. using 96·9 per cent. acid.
Time of addition: 90 min. Time of stirring: 30 min.

Run Number.	Isobutane : Diisobutene Ratio.	On Olefine Taken, %.	Product >27° C. A.S.T.M. Distillation. I.B.P. °C.	2%.	5%.	10%.	20%.	30%.	40%.	50%.	60%.	70%.	80%.	90%.	F.B.P. °C.	T.D., %.	Residue, %.	Product 27–185° C. On Olefine Taken, %.	Bromine Number. §	Sp. gr. at 15·6° C.	Octane Rating. 50% in H.O.S. ‖	Neat.	+1·5 c.c. T.E.L./(Imp.) gal.	Residue. On Olefine Taken, %.	Bromine Number. §	Sp. gr. at 15·6° C.
42▲	1 : 1	165	38	45·5	53	66·5	94	105	112·5	117·5	125·5	137·5	160·5	197	257	97·5	1·5	136	<1	0·705	71·2	90·5	98	22	14	0·783
51*	1 : 1	167	35·5	50	63·5	78·5	98·5	108	114·5	120·5	128·5	140	165	200	264·5	97·5	1·5	142	<1	0·701	71·6	90·8	99·2	19·6	10	0·782
55	2 : 1	184	33	39	49	64	89	101	107	112	118·5	128	148	194	230	96·5	1	158	<1	0·700	71·1	91·3	98·9	14·8	9·5	0·782
59	4 : 1	190†	36·5	55	68	81	96·5	103	107	110·5	114·5	120	133·5	172	220	97·5	1·5	167‡	<1	0·705	72·3	92·2	101	10·8	10	0·777

* Repeat run with improved stirrer.
† An engine test on the product boiling over 27° C. (*i.e.*, including the residue) gave 90·6 octane number and +1·5 c.c. T.E.L./(Imp.) gal. 100 octane number.
‡ Sulphur 0·01 per cent.
§ Francis method.
‖ High octane standard. A straight-run Iranian cut 52·5 O.N.

the product is also slightly inferior in octane rating. At −10° C., while there is slight improvement in the octane rating of the product, the yield is appreciably lower and a considerable amount of high-boiling residue is formed.

Variation in the ratio of the reactants produces a greater and more useful effect, as can be seen from Table II in which the results obtained when an increased proportion of *iso*butane to olefine is employed. Not only does

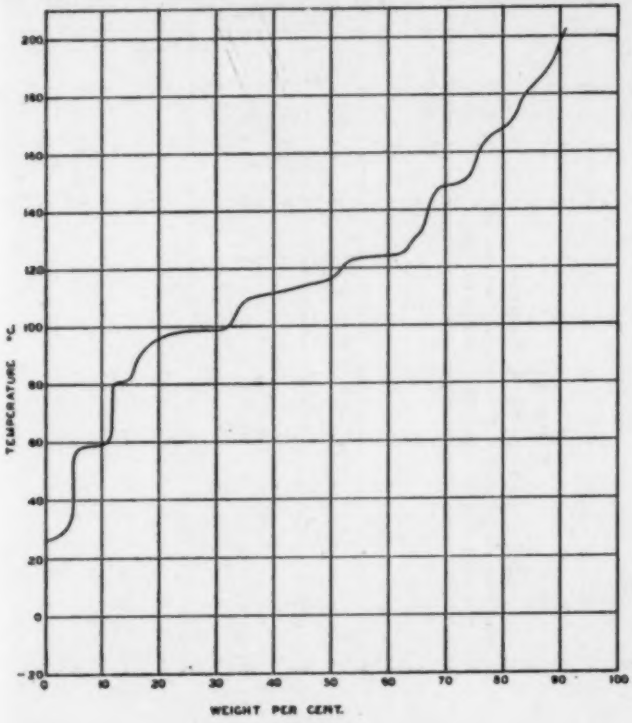


FIG. 2.

DISTILLATION CURVE (25-PLATE COLUMN) OF PRODUCT FROM DI*ISO*BUTENE AND *ISO*BUTANE AT 20° C.

$(C_4H_8)_2 : C_4H_{10}$. Ratio 1 : 2. Run 59.

an excess of the *iso*paraffin over that required for equimolecular proportions of *iso*butane to "*iso*butene" lead to an increased yield, but there is also considerable reduction in the amount of high-boiling residue.* At the same time a definite increase in the octane rating of the fraction boiling between 27 and 185° C. occurs and the crude product distilled through a

* The crude product obtained when using a 4 : 1 ratio of *iso*butane : "*iso*butene" actually had a final boiling point of 220° C. and an octane rating of 90·6 O.N., which, on the addition of 1·5 c.c. T.E.L. per (Imp.) gal., rose to 100·0 O.N.

25-plate column shows a considerable increase in the *iso*-octane fraction (Figs. 2 and 3. Cf. also Fig. 4).

The acid concentration is a factor of considerable importance, and good results are obtained only when it is sufficiently high to bring about vigorous polymerization of the olefine. For most of the latter examined the commercial acid, containing 97 per cent. sulphuric acid, proved entirely satisfactory, and it was only when, as already mentioned, a much less easily polymerized olefine, such as propylene, was employed, that slightly

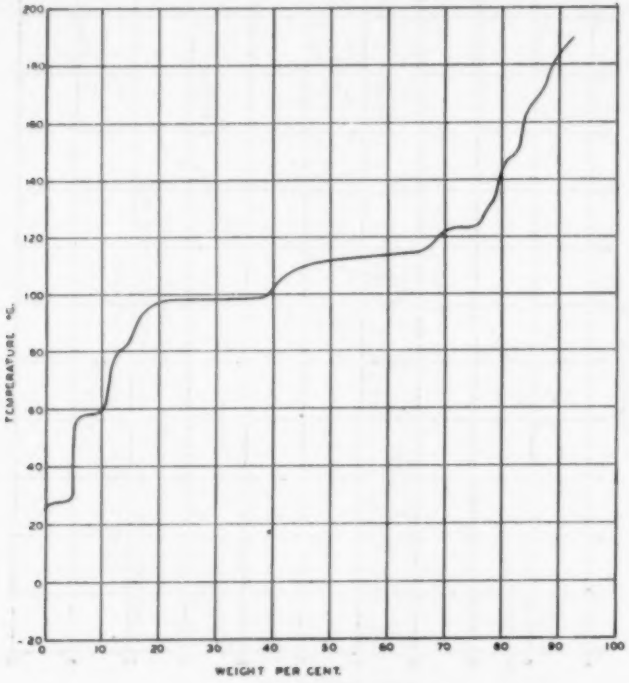


FIG. 3.

DISTILLATION CURVE (25-PLATE COLUMN) OF PRODUCT FROM DI*ISO*BUTENE AND EXCESS *ISO*BUTANE AT 20° C.

$(C_4H_8)_2 : C_4H_{10}$. Ratio 1 : 8. Run 63.

higher concentrations were necessary. Too high a concentration invariably leads to considerable oxidation, with resultant sulphur dioxide formation and charring; the yield is then appreciably lower, and has an inferior octane rating. On the other hand, the effectiveness of the acid falls away comparatively rapidly when the concentration falls below the optimum. This can be to some extent overcome by employing a somewhat higher temperature for the reaction, but even then the results obtained are not satisfactory. Thus, the yield of the 27–185° C. fraction amounted to only 120 per cent. (based on the di*iso*butene taken) when 90 per cent. acid was

employed in the reaction with *iso*butane at 50° C. and the octane rating was only 87 octane number. The presence of traces of unsaturated hydrocarbons was shown by the bromine number (4), which in the case of the residue proved, as anticipated, to be exceptionally high (55). Sulphur-dioxide formation in this reaction was very marked.

The dilution of the acid by the reaction products does not appear to have

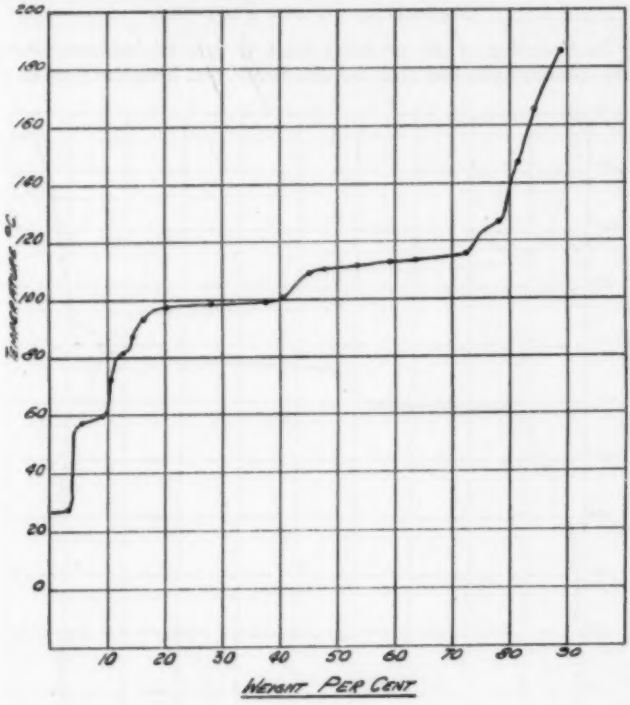


FIG. 4.

DISTILLATION CURVE (25-PLATE COLUMN) OF PRODUCT FROM *iso*BUTENE AND EXCESS *iso*BUTANE AT 20° C.

$C_4H_8 : C_4H_{10}$. Ratio 1 : 4. Run 129.

nearly such an adverse effect as when water is the diluent. Since the nature of these products is quite unknown, a satisfactory analysis of the acid at the end of the reaction is not possible, dilution of the acid with ice-water apparently bringing about decomposition, with the formation of a highly unsaturated oil of high gravity, possibly similar to those obtained by Ipatiev and Pines (*J. Org. Chem.*, 1936, **1**, 477) from the action of sulphuric acid on di*iso*butene. As far as can be judged, however, the amount of water formed in the reaction is not great, and organic products constitute the main diluents.

The effect of varying the time taken to add the olefine and during which

agitation is continued when the addition is completed was not found to be great, and the optimum conditions are probably determined by the apparatus. It was, however, observed that the vigour of the agitation has an appreciable effect, extremely vigorous agitation giving a higher yield of useful material of improved octane rating.

Composition of the Products.

The fractionation of the products from di- and tri-*iso*butene through a 25-plate column indicated that definite individual hydrocarbons or groups

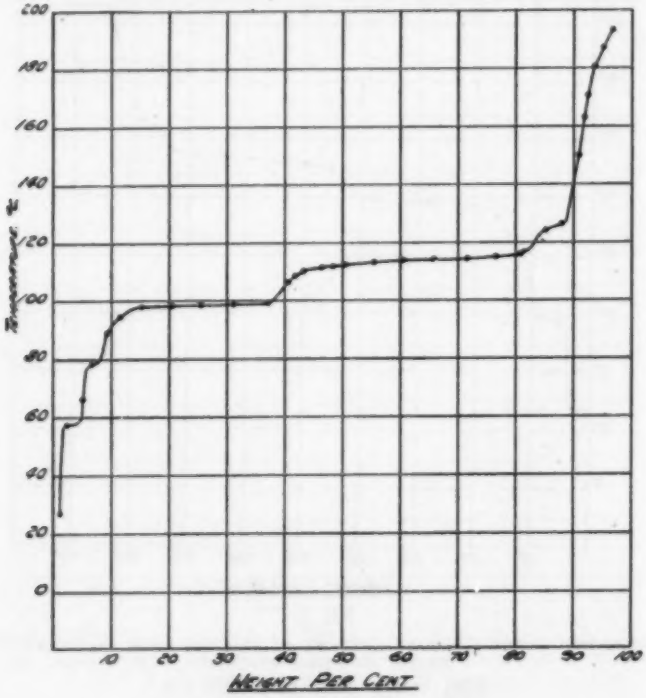


Fig. 5.

Distillation curve (25-plate column) of product from butene-2 and excess *iso*butane at 20° C.

$C_4H_8 : C_4H_{10}$. Ratio 1 : 4. Run 121.

of hydrocarbons were present in both, and that these were identical. The relative proportions in which they are present, however, is determined by reaction conditions, particularly by the ratio of *iso*paraffin to olefine employed. Under similar conditions of reaction there is such a remarkable similarity between the distillation curves of the products that they are practically super-imposable.

Amongst the hydrocarbons so far identified, are *iso*pentane, 2 : 3-dimethylbutane, 2 : 3- and 2 : 4-dimethylpentanes, 2 : 2 : 4-trimethylpentane, 2 : 5-dimethylhexane and 2 : 2 : 5-trimethylhexane. Several other hydrocarbons have been isolated, but their identification has not yet been possible owing to the lack of reliable data concerning the physical properties of the higher-boiling paraffins. No indications have been obtained at any time of the presence of normal paraffins in the products from any of these

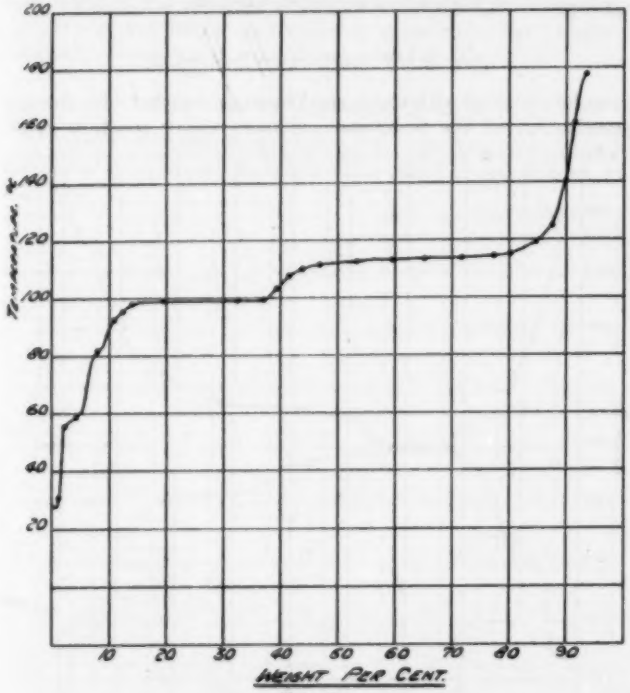


FIG. 6.

DISTILLATION CURVE (25-PLATE COLUMN) OF PRODUCT FROM BUTENE-1 AND EXCESS *iso*BUTANE AT 20° C.

$C_4H_8 : C_4H_{10}$. Ratio 1 : 4. Run 123.

reactions which, as already stated, appear to be entirely *iso*paraffinic in composition.

THE BUTENE–*iso*BUTANE REACTION.

The addition of butene-2, prepared by the dehydration of *sec.*-butyl alcohol, and containing approximately 0·5 per cent. *iso*butene, to *iso*butane proceeds smoothly in the presence of 97 per cent. acid at 20° C. The reaction product closely resembles that obtained in similar circumstances from *iso*butene, both in yield and octane rating, whilst the distillation curve (Fig. 5) obtained by means of a 25-plate column appears to indicate

the presence of similar hydrocarbons or groups of hydrocarbons. This surprising conclusion has not yet been completely proved, as time has not permitted the identification of all the hydrocarbons formed. There is, however, no doubt that considerable quantities of 2 : 2 : 4-trimethylpentane are produced.

Similar results were obtained with butene-1, although the reaction did not proceed quite so readily as with butene-2. The quantity and quality of the product were, however, comparable (Fig. 6).

The B.I.B.–*iso*Butane Reaction.

The results obtained with the normal butenes, coupled with the apparent depolymerization of the *iso*butene polymers under reaction conditions,

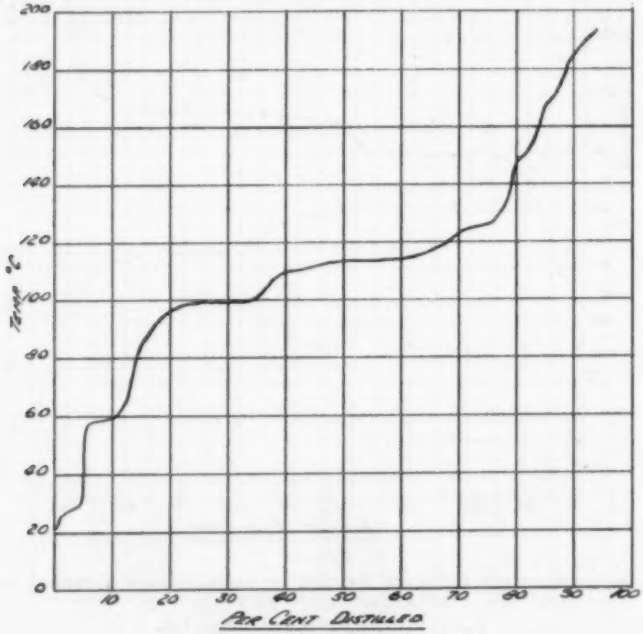


Fig. 7.

DISTILLATION CURVE (25-PLATE COLUMN) OF PRODUCT FROM OCTENE FRACTION OF BUTENE–*iso*BUTENE MIXED POLYMER AND *iso*BUTANE AT 20° C.

$C_4H_{10} : C_4H_{10}$. Ratio 1 : 8. Run 72.

suggested that the di*iso*butene might effectively be replaced by the butene–*iso*butene addition product. Such a reaction, if successful and with a satisfactory product, would, owing to the much higher yield of B.I.B. obtainable from a definite quantity of C_4 cut, increase very considerably the potential supply of 90 octane fuel.

Preliminary experiments carried out on a B.I.B. cut boiling over the range

105·5–112° C. using 97 per cent. acid at 20° C. were found to proceed normally, yielding a saturated product of good octane rating, although both yield and octane rating were slightly lower than those obtained from di*iso*butene under corresponding conditions. Both were considerably improved, however, in later experiments when a wider B.I.B. cut was used. Eventually it was found that by employing a B.I.B. cut, b. pt. 95–180° C., and a 4 : 1 ratio of *iso*paraffin to "butene," a satisfactory yield of 90 octane material was obtained. As was anticipated, fractionation of this product gave a distillation curve closely resembling that obtained from the *iso*butene polymers and normal butenes (Fig. 7).

The Use of Refinery C_4 Cuts.

The C_4 fraction obtained from cracking or reforming operations consists of a mixture of straight and branched chain paraffins and olefines, in which

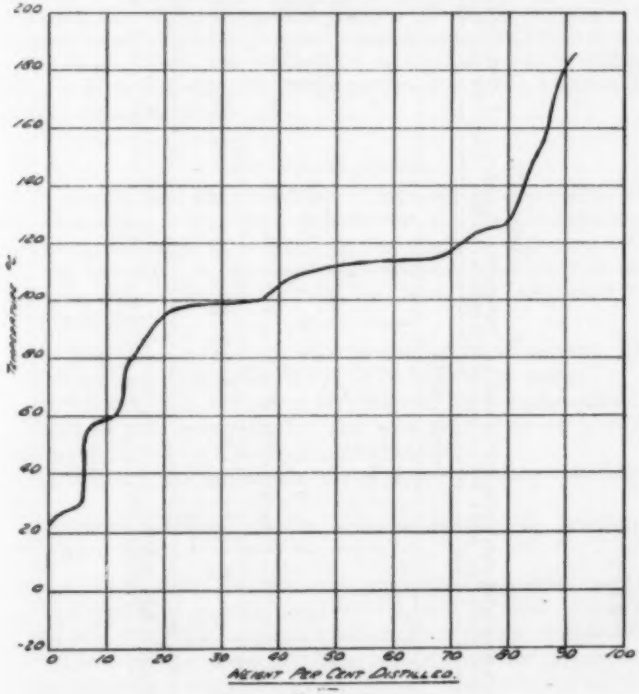


Fig. 8.

Distillation curve (25-plate column) of product from unsaturated C_4 cut and excess *iso*butane (69 per cent. concentrate) at 20° C.

Unsaturated hydrocarbon : *iso*butane ratio 1 : 3. Run 150.

the normal hydrocarbons predominate, together with a small amount of butadiene. Since, with the exception of the butadiene, the individual

TABLE III.

Unsaturated C_4 cut from cracking unit stabilizers. Ratio olefine : isobutane 1 : 3.* Saturated C_4 cut (60 per cent. isobutane).
Temperature : 20° C. Acid : 96·9 per cent. Time of addition : 90 min. Time of stirring : 30 min.

Run Number.	Product >27° C.														Product 27–185° C.				Residue >185° C.	
	Based on Olefines Taken, %.	Sp. gr. 15·6° C.	Bromine Number (French).	I.B.P. ° C.	2%.	5%.	10%.	20%.	30%.	40%.	50%.	60%.	70%.	80%.	90%.	F.B.P. ° C.	Based on Olefines Taken, %.	Sp. gr. 15·6° C.	Bromine Number (French).	Octane Rating. Neat.	Octane Rating. Neat + 1 c.c. T.E.L./per (Imp.) gal.	Based on Olefines Taken, %.	Sp. gr. 15·6° C.	Bromine Number (French).
1501*	178	0·699	1	34	46	56·5	73	94	102	106	108·5	112	113	129	183	229	162	0·698	<1	90·7	98·0	16	0·781	15
1191†	165	0·703	2	57	67	78	88	97·5	102	105	107·5	110·5	115	121	146	218	153	0·701	<1	91·8	99·7	11	0·795	24

* The quantities of these fractions were selected to give an olefine : isobutane ratio of 1 : 3, due allowance being made for the isobutane content of the unsaturated material.
† Unsaturated C_4 cut from H.P. cracking unit. Unsaturated content 57 per cent. Butadiene 3·6 per cent.
‡ Unsaturated C_4 cut from L.P. cracking unit. Unsaturated content 95 per cent. Butadiene 22·7 per cent. Recovered butane contained less than 0·2 per cent. butadiene.

unsaturated hydrocarbons have been shown to react satisfactorily with *iso*butane in the presence of acid, the possibility of utilizing the C_4 fraction was investigated. It was at first thought that the butadiene present would have a deleterious effect by forming high-boiling polymers and tarry by-products, and methods were therefore considered for its removal. A preliminary experiment with a C_4 cut taken directly from the stabilizer containing approximately 50 per cent. unsaturated hydrocarbons (butadiene 3·6 per cent.) was, however, made, and found to give an entirely satisfactory product, the butadiene apparently producing no ill effects. This result was confirmed in later experiments—in fact, it was found that a C_4 fraction containing as high as 20 per cent. of butadiene could be used without giving trouble.

In place of the pure *iso*butane used in the earlier work, a concentrate containing 70 per cent. was tried with entirely satisfactory results, and this material was consequently used for most of the later experiments (Fig. 8).

The importance of these results is obvious. It enables a good yield of a 90 octane *iso*paraffinic fuel to be produced in one operation from the reaction, under simple conditions, of a crude C_4 fraction taken from a cracking plant stabilizer with a concentrated *iso*butane fraction using a cheap readily available condensing agent.

100 Octane Fuels.

At the present time the production of high-octane *iso*paraffins suitable for 100 octane fuels is dependent on *iso*butene, and the potential supply of such blending materials determined by the supply of *iso*butene available.

With the discovery of the *iso*paraffin addition reaction, five methods of producing high-octane *iso*paraffinic fuel from this isobutene * became available namely,

(1) Acid polymerization to di*iso*butene (cold-acid process), followed by hydrogenation to *iso*-octane (2 : 2 : 4-trimethylpentane);

(2) Selective polymerization also followed by hydrogenation;

(3) Acid polymerization by cold acid process to di- and tri-*iso*-butenes followed by reaction with *iso*butane;

(4) Selective polymerization followed by reaction with *iso*butane, and

(5) Direct addition of the *iso*butene-bearing C_4 fraction with *iso*butane.

The products from all these processes consist of *iso*paraffins, but there is considerable variation in the yields both in amount and octane rating. Since, however, a greatly increased yield may more than compensate for a product of lower octane rating, the value of any particular process can only be assessed by taking both into consideration. The following table shows the potential yield of high-octane *iso*paraffins producible by the five processes, together with their octane ratings.

* Since the normal butenes, propylene and trimethylethylene are all capable of yielding suitable blending materials for 100 octane aviation fuels when condensed with *iso*butane, the potential supply of such fuels is no longer dependent on *iso*butene, and is therefore considerably increased. The determining factor becomes then *iso*-butane rather than *iso*butene.

By blending with tetraethyl lead and a special cut of Iranian gasoline, 70 O.N., the following relative quantities of 100 octane fuel may be produced.

TABLE IV.

Yields of High Octane isoParaffins available from C_4-Olefines and their Polymers or Co-Polymers.

	(*a*) From Di*iso*-butene by Hydro-genation.	(*b*) From Poly*iso*-butenes and *iso*-Butane.	(*c*) From B.I.B. by Hydro-genation.	(*d*) From B.I.B. and *iso*-Butene.	(*e*) From C_4-cut and *iso*-Butane.
Yields per unit of *iso*-butene . . .	0·7	1·5 (*f*)	1·5	2·3 (*f*)	4·2 (*f*)
Octane number, C.F.R. motor method . .	98–100	92	95	91	91

(*a*) Based upon 70 per cent. conversion of *iso*butene to di*iso*butene.
(*b*) The crude acid polymerization product may be used.
(*c*) Based upon a conservative conversion figure of 1·8. An 85 per cent. fraction (b. pt. 95–120° C.) thus gives 1·5 for the useful product.
(*d*) Based on an 85 per cent. fraction. A correspondingly higher yield is possible by taking a wider fraction (b. pt. 95–180° C.).
(*e*) C_4-cut ex H.P. cracking units. Total unsats. 56 per cent, *iso*butene 20 per cent.
(*f*) The figures in the second, fourth and fifth columns are based on an economical acid consumption.

TABLE V.

Yield of 100*-Octane Gasoline based on Unit Quantity of* iso*Butene.*

	From D.I.B. by Hydro-genation.	From Poly*iso*-Butenes and *iso*-Butane.	From B.I.B. by Hydro-genation.	From B.I.B. and *iso*-Butane.	From C_4-cut and *iso*-Butane.
Yield of 100-octane gasoline per unit of *iso*-butene . . .	1·27	2·0	2·5	3·1	5·6
Composition :					
*iso*Paraffin base .	55	75	60	75	75
Gasoline cut * . .	45	25	40	25	25
T.E.L./gal. (Imp.) .	3·5	2·6	2·9	2·6	2·6

* Octane number 70 (C.F.R. motor method).

We wish to record our thanks to the Chairman of the Anglo-Iranian Oil Co., Ltd., for permission to publish these results.

THE VISCOSITIES OF HYDROCARBONS.

By E. B. Evans, Ph.D., M.Sc. (Member).

PARTS IV–VI.* †

Synopsis.

Previous parts of this paper covered the general scope of the investigation, consideration of the small viscometers used for measuring hydrocarbon viscosities and discussion of the viscosities of the normal paraffin hydrocarbons. On thirteen of these hydrocarbons, there exist data sufficiently reliable and extensive to enable absolute and kinematic viscosities to be tabulated showing, in most cases, values at 0° C., 20° C., 50° C., 80° C. and 100° C. Part IV describes the *iso*paraffin hydrocarbons, of which eighteen have been sufficiently well examined to permit tabulation. The monocyclic naphthenes recorded include twenty-one *cyclo*pentane and *cyclo*hexane derivatives with from five to thirty-two carbon atoms; fourteen *cyclo*pentane and *cyclo*hexane hydrocarbons have been examined by the author (details of preparation and physical properties being included in the paper) and four long-chain *cyclo*hexane derivatives (twenty-four to thirty-two carbon atoms) have been recorded by Mikeska (1936).

Data on the acyclic olefines (in Part VI (*a*) are tabulated seventeen hydrocarbons) include the earlier results of Thorpe and Rodger and measurements on three hydrocarbons (di*iso*butylene, *n*-dodecene-1 and *n*-hexadecene-1) which have not previously been examined for viscosity. Our knowledge of the viscosities of the olefines of higher molecular weight is due to the work of Lerer and, particularly, of Landa and his collaborators. The latter work is noteworthy by reason of the completeness of the data, viscosity measurements being recorded for 10° C. intervals over an adequate temperature range, and full density and other physical data given. Viscosity results on the cyclic olefines are few, only single measurements existing on about ten of these hydrocarbons. For *cyclo*hexene, however, our own results extend from 5° C. to 75° C.

PART IV.

The Viscosities of the *iso*Paraffins.

Unfortunately no series of the isomeric paraffins has been investigated thoroughly, even that of the hexanes, which is the most extensive, being far from complete. There are altogether five isomeric hexanes, of which *n*-hexane has already been discussed under the normal paraffins. Thorpe and Rodger (*loc. cit.*) have made a complete series of measurements of 2-methylpentane up to about 55° C. The four *iso*hexanes have been examined by Chavanne and van Risseghem,[19] but these cover only the range from 0° C. to 30° C.; the values for 2-methylpentane are in fairly good agreement with those of Thorpe and Rodger, differing by 3 per cent. at 20° C. A very accurate series of measurements on all the isomeric heptanes have been recorded by Edgar, Calingaert and Marker,[20] but these are at only one temperature, 20° C. Thorpe and Rodger examined 2-methylhexane over a wide range of temperature, and the value of 0·381 at 20° obtained by plotting their results agrees well with that of 0·378, given by Edgar and his collaborators. There are a number of other measurements on the lower *iso*paraffins recorded, and these are given in the Tables XIII and XIV.[21]

* Paper received February 8th, 1938.

† For Parts I–III see *J. Instn Petrol. Tech.*, 1938, **24** (171), 38–53.

TABLE XIII.

Thorpe and Rodger.		Thorpe and Rodger.		Bingham, White, Thomas and Caldwell.		Ubbelohde and Agthe.		Landa and Kejvan.		Riedl.		Habada.	
2-Methylpentane.		2-Methylhexane.		2 : 7-Dimethyloctane.		Diisoamyl.		2 : 1-Dimethyldodecane.		2-Methylheptadecane.		Diethyl-3 : 12-tetradecane.	
T.	η.	T.	η.	T.	η.	T.	η.	T.	η.	T.	η.	T.	η.
0·61	0·3688	0·42	0·4743	25	0·8278	20	0·817	0	2·608	0	—	0	9·010
5·59	0·3487	7·70	0·4343	35	0·6702	40	0·658	10	1·945	10	5·309	10	6·337
10·25	0·3316	15·88	0·3959	50	0·5540	60	0·518	20	1·549	20	3·956	20	4·700
15·26	0·3147	24·63	0·3607	65	0·4686	80	0·427	30	1·205	30	3·011	30	3·635
20·51	0·2987	32·31	0·3333			100	0·355	40	1·021	40	2·374	40	2·887
25·45	0·2841	40·05	0·3092					50	0·854	50	1·916	50	2·355
31·97	0·2670	49·01	0·2839					60	0·724	60	1·576	60	1·959
36·63	0·2550	56·46	0·2651					70	0·632	70	1·331	70	1·667
41·07	0·2450	63·92	0·2484					80	0·554	80	1·132	80	1·435
45·38	0·2355	71·84	0·2316					90	0·492	90	0·985	90	1·263
51·17	0·2235	80·66	0·2149					99	0·439	100	0·874	99	1·134
55·43	0·2151	88·41	0·2012										

Landa and Sliva.		Kejvan.		Čech and Sliva.		Riedl.		Čech and Sliva.		Lerer.			
3-Ethyloctadecane.		2 : 19-Dimethyleicosane.		4-Propylnonadecane.		2-Methyltricosane.		5-Butyleicosane.		7 : 12-Dimethyl-n-dihexyl-(9 : 10)-octadecane.		7 : 16-Dimethyl-9 : 11 : 12 : 14-tetra-n-hexyldocosane.	
T.	η.	T.	η.	T.	η.	T.	η.	T.	η.	T.	η.	T.	η.
0	11·548	—	—	0	18·902	—	—	0	—	16	42·6	25	161
10	7·884	—	—	10	10·998	—	—	10	19·521	27	26·7	37	79·5
20	5·607	—	—	20	8·807	—	—	20	12·913	38·5	16·9	61	25·0
30	4·165	—	—	30	6·453	—	—	30	9·047	62·0	7·9	80	13·0
40	3·200	41	3·535	40	4·854	—	—	40	6·641	71·5	5·5		
50	2·541	50	2·811	50	3·827	50	4·550	50	5·060				
60	2·085	60	2·245	60	3·061	60	3·495	60	3·965				
70	1·748	70	1·819	70	2·534	70	2·795	70	3·213				
80	1·477	80	1·512	80	2·148	80	2·287	80	2·654				
90	1·256	90	1·267	90	1·843	90	1·918	90	2·449				
99	1·1013	—	—	99	1·615	100	1·632	99	1·976				

TABLE XIV.

Hydrocarbon.	0°.	15°.	20°.	25°.	30°.	Author.
isoPentane . . .	0·274	0·238	—	—	—	Timmermans and Martin
2-Methylpentane . .	0·371	0·324	0·310	0·295	0·280	Chavanne and van Risseghem
3-Methylpentane . .	0·394	0·339	0·322	0·307	0·292	
2 : 2-Dimethylbutane .	0·477	0·397	0·375	0·351	0·330	
2 : 3-Dimethylbutane .	0·495	0·409	0·385	0·361	0·342	
2-Methylhexane . .	—	—	0·378	—	—	Edgar, Calingaert and Marker
3-Methylhexane . .	—	—	0·372	—	—	
3-Ethylpentane . .	—	—	0·377	—	—	
2 : 2-Dimethylpentane .	—	—	0·385	—	—	
2 : 3-Dimethylpentane .	—	—	0·406	—	—	
2 : 4-Dimethylpentane .	—	—	0·361	—	—	
3 : 3-Dimethylpentane .	—	—	0·454	—	—	
2 : 2 : 3-Trimethylbutane .	—	—	0·585	—	—	
2 : 2 : 3-Trimethylbutane .	0·802	0·634	0·599	0·549	0·506	Chavanne and van Risseghem
2 : 2 : 4-Trimethylpentane	—	—	0·503	—	—	Smyth and Stoops

There is also a single value for 2 : 2 : 4-trimethylpentane at 20° by Smyth and Stoops,[22] whose value, 0·503, is in good agreement with that obtained by plotting our own results on this compound over the range 5–90°—viz., 0·502.

Very interesting are the results of Landa and his collaborators on the higher *iso*paraffins with from fourteen to twenty-four carbon atoms,[23] and on two compounds of high molecular weight and with thirty-two and forty-eight carbon atoms, respectively, by Lerer.[24] Some of these compounds have viscosities in the light lubricating oil range.

The only *iso*paraffin examined in this work was *iso*-octane (2 : 2 : 4-trimethylpentane), the details of preparation and properties of which are as follows :

iso-*Octane* (2 : 2 : 4-*trimethylpentane*.)—*iso*-Octane was purified by treating the material supplied as a knock-rating standard with 99 per cent. sulphuric acid, washing, drying and fractionating. The physical constants are compared with those given by Edgar, Calingaert and Marker.[25]

	Our Sample.	Edgar, etc.
B. pt. (corr.), ° C. . . .	99·2	99·3
d_4^{20}	0·6921	0·6918
d_4^{30}	0·6680	—
n_D^{20}	1·3917	1·3916
A. pt., ° C.	79·5	—

TABLE XV.

New Data.

Hydrocarbon.	5° C.	15° C.	30° C.	45° C.	60° C.	75° C.	90° C.
2:2:4-Trimethylpentane .	0·6077	0·5344	0·4472	0·3802	0·3270	0·2839	0·2478

PART V.

THE VISCOSITIES OF THE MONOCYCLIC NAPHTHENES.

Chavanne and van Risseghem [26] investigated seven hydrocarbons of the *cyclo*pentane and *cyclo*hexane series over the range from 0° to 30°, including the parent hydrocarbons, the two methyl derivatives and the three dimethyl*cyclo*hexanes. The last compounds were prepared by hydrogenation of the aromatics, using both nickel and platinum catalysts, and the resulting products had very different viscosities in the two sets of cases. The differences are due to *cis–trans* isomerism, but data on the physical properties of the pure isomers are so scanty that it is not possible to say with any accuracy what is the composition of the preparations. In general, the values obtained here for preparations of the dimethyl*cyclo*hexanes from Rhone–Poulenc are quite close to those for Chavanne's nickel preparations, and these probably consist mainly of *cis*-isomers. As is remarked later, the *meta*- and *para*-dimethyl*cyclo*hexanes examined here are almost identical in density, boiling point, refractive index and aniline point, but they differ considerably in freezing point and in viscosity.

TABLE XVI.

Viscosities of iso*Paraffins.*

Hydrocarbon.	Empirical Formula.	Mol. Wt.	Viscosity in cp. at					Source of Data.
			0° C.	20° C.	50° C.	80° C.	100° C.	
2-Methylpentane	C_6H_{14}	86	0·3735	0·2985	0·226	0·1795	—	Thorpe and Rodger
3-Methylpentane	C_6H_{14}	86	0·394	0·322	0·2465	—	—	Chavanne and van Risseghem
2 : 3-Dimethylbutane	C_6H_{14}	86	0·4945	0·3835	—	—	—	
2 : 2-Dimethylbutane	C_6H_{14}	86	0·477	0·3735	—	—	—	
2-Methylhexane	C_7H_{16}	100	0·4765	0·381	0·2825	0·217	0·1815	Thorpe and Rodger
2 : 2 : 3-Trimethylbutane	C_7H_{16}	100	0·8015	0·5915	—	—	—	Chavanne and van Risseghem
2 : 2 : 4-Trimethylpentane	C_8H_{18}	114	0·647	0·5025	0·359	0·269	0·227	Author
2 : 7-Dimethyloctane	$C_{10}H_{22}$	142	1·047	0·8205	0·5755	0·4285	0·3595	Ubbelohde and Agthe
2 : 11-Dimethyldodecane	$C_{14}H_{30}$	198	2·630	1·531	0·851	0·555	0·4365	Landa and Kejvan
2-Methylheptadecane	$C_{18}H_{38}$	254	7·638	3·963	1·919	1·143	0·875	Landa and Riedl
3 : 12-Diethyltetradecane	$C_{18}H_{38}$	254	9·010	4·700	2·355	1·437	1·122	Landa and Habada
3-Ethyloctadecane	$C_{20}H_{42}$	282	11·61	5·598	2·553	1·466	1·089	Landa and Sliva
2 : 12-Dimethyleicosane	$C_{22}H_{46}$	310	—	6·457	2·818	1·514	0·9955	Landa and Kejvan
4-Propylnonadecane	$C_{22}H_{46}$	310	18·90	8·807	3·827	2·148	1·600	Landa, Čech and Sliva
2-Methyltricosane	$C_{24}H_{50}$	338	—	13·24	4·550	2·280	1·629	Landa and Riedl
5-Butyleicosane	$C_{24}H_{50}$	338	—	12·91	5·060	2·654	1·950	Landa, Čech and Sliva
7 : 12-Dimethyl-*n*-dihexyl-(9 : 10)-octadecane	$C_{32}H_{66}$	450	—	35·81	11·32	5·129	—	Lerer
7 : 16-Dimethyl-9 : 11 : 12 : 14-tetra-*n*-hexyldocosane	$C_{48}H_{98}$	678	—	227·5	39·9	13·12	(7·762)	

TABLE XVII.

Kinematic Viscosities—iso Paraffins.

Hydrocarbon.	d_4^0.	d_4^{50}.	d_4^{100}.	Viscosity in cs. at				
				0° C.	20° C.	50° C.	80° C.	100° C.
2-Methylpentane	0·6711	0·6284	0·5857	0·5565	0·4565	0·3596	0·2980	—
3-Methylpentane	0·6819	0·6389	0·5959	0·5780	0·4845	0·3860	—	—
2 : 3-Dimethylbutane	0·6794	0·6354	0·5914	0·7276	0·5795	—	—	—
2 : 2-Dimethylbutane	0·6677	0·6284	0·5831	0·7142	0·5750	—	—	—
2-Methylhexane	0·6960	0·6533	0·6106	0·6845	0·5610	0·4325	0·3455	0·2975
2 : 2 : 3-Trimethylbutane	0·7068	0·6648	0·6228	1·134	0·8575	—	—	—
2 : 2 : 4-Trimethylbutane	0·7081	0·6680	0·6279	0·9135	0·7260	0·5375	0·4180	0·3615
2 : 7-Dimethyloctane	0·7390	0·7005	0·6621	1·417	1·132	0·8215	0·6325	0·5430
2 : 11-Dimethyldodecane	0·7820	0·7484	0·7130	3·363	1·991	1·137	0·7630	0·6120
2-Methylheptadecane	0·7946	0·7593	0·7243	9·574	5·078	2·527	1·548	1·208
3 : 12-Diethyltetradecane	0·8059	0·7722	0·7385	11·18	5·932	3·049	1·911	1·519
3-Ethyloctadecane	0·8091	0·7750	0·7421	14·35	7·039	3·294	1·941	1·468
2 : 10-Dimethyleicosane	0·8083	0·7757	0·7431	—	8·119	3·633	2·002	1·340
4-Propylnonadecane	0·8109	0·7771	0·7440	23·31	11·05	4·925	2·835	2·150
2-Methyltricosane	0·8146	0·7827	0·7508	—	16·51	5·813	2·986	2·169
5-Butyleicosane	0·8150	0·7815	0·7498	—	16·12	6·474	3·478	2·600
7 : 16-Dimethyl-9 : 11 : 12 : 14-tetra-*n*-hexyldocosane	0·9014	0·8689	0·8364	—	256·1	45·92	15·45	9·281

Ubbelohde and Agthe [21] determined the viscosities of ethyl*cyclo*hexane, 1 : 3 : 5-trimethyl*cyclo*hexane and *iso*butyl*cyclo*hexane over the range 20–100° C., but most of the other data previously published consisted either of single measurements or of two or three measurements at comparatively low temperatures and covering a very restricted temperature range.[27] A series of single measurements at 13·5° was made by Godchot and Cauquil [28] on a number of naphthene hydrocarbons, including some *cyclo*heptane and *cyclo*-octane derivatives; it is unfortunate that only one temperature was employed, and that a somewhat unusual one, since there are no other data on compounds with seven- and eight-membered rings.

Mikeska [28a] has prepared and examined a large number of complex hydrocarbons. The data he gives include viscosity measurements in kinematic units, at four or five temperatures. Included in these compounds are four *cyclo*hexane derivatives with long paraffinic side-chains containing eighteen to twenty-six carbon atoms. His data on these hydrocarbons are given in Table XXII, and the results of plotting are included in Tables XXIII and XXIV, which summarize the absolute and kinematic viscosity data on the monocyclic naphthene hydrocarbons.

Our own data cover fourteen monocyclic naphthene hydrocarbons with five- or six-membered rings, and extend over the range 5–90°, except in three cases, where the boiling point of the compound is too low to permit this. Six of the compounds have not previously been examined for viscosity at all, and data on most of the others have usually been confined to one or two measurements at low temperatures. Thus data on the ethyl-, dimethyl-, *n*-propyl-, and *n*-butyl-*cyclo*pentanes and on the *n*-propyl- and *n*-butyl-*cyclo*hexanes are quite new. The details of preparation and properties of these hydrocarbons are given later.

The agreement between these data and the most reliable in the literature is in general excellent. Thus the data of Timmermans and Martin on the two *cyclo*hexane derivatives is quite satisfactory. When Chavanne's data on *cyclo*hexane at 15°, 20° and 30° are plotted against temperature, it is found that a straight line passes through the three points obtained,

instead of the curve which is typical of the usual relation of viscosity and temperature. Ubbelohde and Agthe's results plot irregularly, except in the case of *iso*butyl*cyclo*hexane, which gives a fairly smooth curve. The values given by these authors for ethyl*cyclo*hexane are not in good agreement with our results, and, moreover, give an irregular plot. Our own data give a smooth curve, when viscosity is plotted against temperature.

The Preparation of *cyclo*Pentane Hydrocarbons.

The starting material for most of the *cyclo*pentane hydrocarbons was adipic acid. Seven kilos of the acid were distilled in 300-gm. lots from a pyrex distilling flask heated in a metal bath maintained at 285–295° C. (the alloy used was a mixture of 37 per cent. lead and 63 per cent. tin), with the addition of 15 gms. of finely powdered barium hydroxide to each portion.[29] The distillation was completed in about 6 hours, and the light-coloured oil separated from the water formed, washed with soda to remove unchanged adipic acid, and fractionated. The total yield of *cyclo*pentanone was about 69 per cent. theoretical and was a very light-coloured liquid boiling at 130·7° C. (corr.).

Part of the *cyclo*pentanone was reduced to *cyclo*pentanol by reduction with sodium and moist ether.[30] Seven hundred grams were reduced in portions of 100 gm., the ketone being dissolved in 400 mls. of ether and floated on a litre of water in a 2-litre flask fitted with a reflux condenser and a side-tube for introducing sodium. The *cyclo*pentanol was recovered in 60 per cent. yield by fractionation of the dried ethereal solution. It boiled at 140·0° C. within a range of 0·5° C., leaving a residue of very viscous material, presumably the pinacone. Attempts to carry out the reduction by hydrogenation with a platinum-black catalyst in absolute alcohol solution were unsuccessful, very little reduction occurring after 24 hours' shaking.

*cyclo*Pentanol (400 gms.) was dehydrated by distilling 100-gm. portions with 150 gms. of granulated anhydrous zinc chloride. The product, after washing and fractionating, gave an 80 per cent. yield of *cyclo*pentane, boiling at about 44·5° C. (corr.).

Hydrogenation to *cyclo*pentane was carried out using the apparatus and method described by Adams.[31] About 220 gms. of *cyclo*pentene were dissolved in an equal volume of glacial acetic acid and placed in a hydrogenating bottle with 1 gm. of platinum catalyst. After evacuation, the bottle was connected with a reservoir containing hydrogen at 40 lb. pressure and shaken at about 550 r.p.m. The catalyst–platinum oxide, prepared by fusing chloroplatinic acid with sodium nitrate as described by Adams—was very quickly reduced to platinum-black, and a very rapid absorption of hydrogen occurred, the pressure drop after 15–20 minutes being almost the theoretical. After an hour the acetic acid solution was removed, the catalyst filtered off, and the acid removed by water and alkali washing. The *cyclo*pentane obtained was shaken with 99 per cent. sulphuric acid to remove possible traces of unchanged *cyclo*pentane, washed and fractionated. The yield was about 80 per cent. (170 gms.), the losses being mainly due to the volatility of the material (b. pt. 49·5° C.).

The methyl-, ethyl-, *n*-propyl- and *n*-butyl-*cyclo*pentanes were obtained as described by Chavanne and Becker [32] by the action of *cyclo*pentanone on the ethereal solution of the appropriate alkyl magnesium halide, dehydrating the alcohol thus obtained and hydrogenating the cyclic olefine to the alkyl*cyclo*pentane. In the case of methyl*cyclo*pentane, for instance, the starting materials were 150 gms. methyl iodide, 23 gms. magnesium turnings and 77 gms. *cyclo*pentanone, a 48 per cent. yield of methyl*cyclo*pentanol being obtained after vacuum distillation of the ether solution. Methyl*cyclo*pentanol is solid at room temperatures, and dehydrates very easily on distillation. In fact, by fractionation of the ethereal solution from the Grignard reaction, at ordinary pressures, a 47 per cent. yield of methyl*cyclo*pentene could be obtained. The methyl*cyclo*pentene was hydrogenated to methyl*cyclo*pentane as described for *cyclo*pentene. The ethyl*cyclo*pentanol and its higher homologues were dehydrated immediately after removal of the ether, and without further purification, by distillation with zinc chloride or *p*-toluenesulphonic acid, the latter giving better yields.

In the preparation of the butyl member of the series, a small amount of *cyclo*pentene and about 50 mls. of pure *n*-octane were isolated, besides 120 gms. of butyl*cyclo*pentene from the distillation products of the dehydration of the crude butyl*cyclo*pentanol. This was not unexpected, in view of the known condensing action of magnesium on certain alkyl halides.

Attempts to prepare *iso*propyl*cyclo*pentanol by the Grignard reaction were unsuccessful, only about 10 gms. of impure product being obtained from 63 gms. of *cyclo*pentanone. Meerwein [33] obtained similar results, and states that the main product of this reaction is 2-*cyclo*propylidene-*cyclo*pentanone.

In the preparation of 1 : 3-dimethyl*cyclo*pentane, the starting point was α-methyladipic acid, which was distilled in three 400 gms. portions at 320° C., using a metal-bath as for adipic acid.[34] The yield of purified 3-methyl*cyclo*pentanone was about 50 per cent. having the following properties: b. pt. (corr.) 141·0° C., $d_4^{15} = 0{\cdot}9272$, $d_4^{20} = 0{\cdot}9226$, $n_D^{15} = 1{\cdot}4370$, $n_D^{20} = 1{\cdot}4351$. This material was converted into 1 : 3-dimethylpentanol by the Grignard reaction with methyl iodide, and the alcohol dehydrated to the olefine, which was hydrogenated in the manner previously described. The yields were very similar to those in analogous reactions. In general, the yields of the purified *cyclo*pentane hydrocarbons were 20–30 per cent., calculated on the weight of *cyclo*pentanone used.

The physical constants of the *cyclo*pentane hydrocarbons are given in Table XVIII. There is some divergence in the physical data recorded in the literature.[35] The data obtained here agree excellently in most cases with those of Eisenlohr.

The Preparation of *cyclo*Hexane Hydrocarbons.

*cyclo*Hexane was purchased from Howards and Sons, Ltd., and purified by treatment with 99 per cent. sulphuric acid, followed by repeated fractionation through a three-foot column packed with ¼-in. Lessing rings. The fraction finally collected boiled over 0·2° C., and although comparison

of its constants indicates that it was not quite pure, its freezing point of 4·5° C. shows, according to the figures of Bruun and Hicks-Bruun,[36] that about 99·5 per cent. *cyclo*hexane was present.

TABLE XVIII.

The Properties of the cyclo*Pentane Hydrocarbons.*

Hydrocarbon.	*cyclo*-Pentane.	Methyl-*cyclo*-pentane.	Ethyl-*cyclo*-pentane.	1 : 3-Dimethyl *cyclo*-pentane.	*n*-Propyl-*cyclo*-pentane.	*n*-Butyl-*cyclo*-pentane.
B. pt. (corr.)° .	49·4 ± 0·5	71·9	103 ± 0·5	90·5	130·6 ± 0·2	157·2
d_4^{15} . . .	0·7498	0·7541	0·7736	0·7504	0·7812	0·7886
d_4^{20} . . .	0·7457	0·7496	0·7695	0·7463	0·7766	0·7847
n_D^{20} . . .	1·4070	1·4099	1·4201	1·4096	1·4269	1·4310
Iodine number .	0·2	0·2	0·3	0	0	1·0
A. pt., °C. . .	16·8	33·0	36·7	46·4	44·5	48·7

TABLE XIX.

The Properties of the cyclo*Hexane Hydrocarbons.*

Hydrocarbon.	*cyclo*-Hexane.	Methyl-*cyclo*-hexane.	Ethyl-*cyclo*-hexane.	*o*-Dimethyl-*cyclo*-hexane.	*m*-Dimethyl-*cyclo*-hexane.	*p*-Dimethyl-*cyclo*-hexane.	*n*-Propyl-*cyclo*-hexane.	*n*-Butyl-*cyclo*-hexane.
B. pt. (corr.)°	80·9 ± 0·1	101·0 ± 0·5	131·6	127·9 ± 1	121·6 ± 1	121·7 ± 1	155·7	180·5 ± 0·5
d_4^{15} . .	0·7820	0·7736	0·7914	0·7912	0·7761	0·7767	0·7968	0·8037
d_4^{20} . .	0·7775	0·7696	0·7875	0·7874	0·7723	0·7727	0·7929	0·8005
n_D^{20} . .	1·4254	1·4239	1·4320	1·4314	1·4255	1·4253	1·4360	1·4410
A. pt. . .	30·2	39·5	43·8	46·3	47·8	47·8	49·8	54·4
F. pt., °C. .	4·5	—	—	—	Below −75	−59	—	—

Methyl*cyclo*hexane was obtained from the same source and similarly purified. The boiling range of the product in this case was about 1° C.; the constants generally are, however, in quite good agreement with those given by Bruun and Hicks-Bruun.[37]

The ethyl-, *n*-propyl- and *n*-butyl-*cyclo*hexanes were prepared by the catalytic hydrogenation of the corresponding aromatics, using the method and apparatus previously described.[38] The hydrogenation was very slow in most cases, up to about 12 hours' shaking being required (the *cyclo*pentenes required from a few minutes to less than an hour), with two or three portions of catalyst in some instances. The reaction went nearly to completion in time, and the last traces of aromatics were removed from the product by sulphonation. The *ortho*-, *meta*- and *para*-dimethyl-*cyclo*hexanes were purchased from Rhone–Poulenc, Paris. These materials are, of course, mixtures of the *cis*- and *trans*-isomers, since the dimethyl-*cyclo*hexanes exhibit the property of stereoisomerism, in common, doubtless, with many other hydrocarbons occurring in petroleum. The properties of the two modifications are, according to Eisenlohr (*loc. cit.*), quite different; the *trans*-isomer is stated to boil some 2 degrees lower than the *cis* form, and the density of the former is also lower. The products from Rhone–Poulenc had boiling ranges of about 2°, and correspond nearly to Eisenlohr's *cis* forms in this respect. The densities are, however, in all cases higher than those of Eisenlohr's *cis* forms. A remarkable

point is that the *meta*- and *para*-compounds—that is, the mixtures of *cis*- and *trans*-isomers—are almost identical as regards density, boiling point, refractive index and aniline point. They differ, however, in their freezing points and viscosities.

The figures given in the literature for the physical constants of the *cyclo*hexane hydrocarbons are not, in general, in very good agreement, differing in the density, for example, by several units in the third decimal place. The ethyl-, *n*-propyl- and *n*-butyl-*cyclo*hexanes, which have been synthesized here, have been very carefully purified and the data may be considered as representing the pure hydrocarbons.

TABLE XX.

Previous Data on Viscosities of Monocyclic Naphthenes.

Hydrocarbon.	Viscosity in cp. at					Author.
	22° C.	—	—	—	—	
*cyclo*Hexane	0·93	—	—	—	—	Drapier, *Bull. Soc. Chim. Belg.*, 1911, 621
	20° C.	40° C.	60° C.	80° C.	100° C.	
Ethyl*cyclo*hexane	0·895	0·649	0·545	0·445	0·354	Engler and Hofer, "Das Erdol," I, 54 (1913)
1:3:5-Trimethyl*cyclo*hexane	0·682	0·520	0·426	0·344	0·306	From unpublished work by Ubbelohde and Agthe
*iso*Butyl*cyclo*hexane	1·223	0·91	0·685	0·5489	0·451	
	0° C.	15° C.	20° C.	25° C.	30° C.	
*cyclo*Pentane	0·572	0·477	0·456	0·427	0·406	Chavanne and van Risseghem, *J. Soc. Chim. Belg.*, 1922, **31**, 87–94.
Methyl*cyclo*pentane	0·665	0·545	0·521	0·484	0·456	
*cyclo*Hexane	—	1·043	0·960	—	0·797	
Methyl*cyclo*hexane	0·976	0·780	—	—	0·627	
o-Dimethyl*cyclo*hexane Pt	1·604	1·195	—	—	0·916	
,, Ni	1·170	0·905	—	—	0·722	
m-Dimethyl*cyclo*hexane Pt	0·874	0·702	—	—	0·578	
,, Ni	0·932	0·750	—	—	0·607	
p-Dimethyl*cyclo*hexane Pt	1·307	0·994	—	—	0·776	
,, Ni	1·05	0·813	—	—	0·655	
	20° C.	29·8° C.	49·8° C.	70° C.	100° C.	
*cyclo*Hexane	0·9705	—	—	—	—	Tausz and Staab, *Petr. Zeit.*, 1930, **26**, 1117.
Methyl*cyclo*hexane	0·7202	—	—	—	—	
Cetyl*cyclo*hexane	—	10·30	5·85	3·74	—	

TABLE XXa.

Hydrocarbon.	Viscosity in cp. at:			Author.
	15° C.	30° C.	60° C.	
*cyclo*Hexane	1·056	0·820	0·534	Timmermans and Martin, *J. Chem. Phys.*, 1927.
Methyl*cyclo*hexane	0·777	0·639	—	
	13·5° C.			
*cyclo*Pentane	0·493	—	—	Godchot and Cauquil, *Compt. rend.*, 1931, **192**, 1560.
Methyl*cyclo*pentane	0·557	—	—	
*cyclo*Hexane	1·127	—	—	
Methyl*cyclo*hexane	0·786	—	—	
1:2-Dimethyl*cyclo*hexane	0·980	—	—	
1:3-Dimethyl*cyclo*hexane	0·738	—	—	
1:4-Dimethyl*cyclo*hexane	0·788	—	—	
1:3:4-Trimethyl*cyclo*hexane	0·934	—	—	
*cyclo*Heptane	1·642	—	—	
Methyl*cyclo*heptane	1·148	—	—	
cyclo-Octane	2·349	—	—	
Methyl*cyclo*-octane	2·797	—	—	

TABLE XXI.

New Data.

Hydrocarbon.	5° C.	15° C.	30° C.	45° C.	60° C.	75° C.	80° C.	100° C.
*cyclo*Pentane	0·5214	0·4634	0·3938	0·3398	—	—	—	—
Methyl*cyclo*pentane	0·6027	0·5342	0·4495	0·3823	0·3273	—	—	—
Ethyl*cyclo*pentane	0·6918	0·6059	0·5069	0·4331	0·3749	0·3286	—	0·2888
1 : 3-Dimethyl*cyclo*pentane	0·6135	0·5419	0·4546	0·3863	0·3337	—	0·2795	—
n-Propyl*cyclo*pentane	0·8429	0·7364	0·6122	0·5188	0·4431	0·3831	—	0·3365
n-Butyl*cyclo*pentane	—	0·9590	0·7794	0·6463	0·5461	0·4673	—	0·4061
*cyclo*Hexane	8° C.) 1·234	1·072	0·8262	0·6522	0·5340	0·4384	—	—
Methyl*cyclo*hexane	0·9131	0·7852	0·6377	0·5272	0·4434	0·3859	—	0·3355
Ethyl*cyclo*hexane	1·061	0·9057	0·7318	0·5893	0·5111	0·4400	—	0·3803
o-Dimethyl*cyclo*hexane	1·203	1·020	0·8153	0·6668	0·5555	0·4706	—	0·4044
m-Dimethyl*cyclo*hexane	0·8486	0·7364	0·6056	0·5071	0·4327	0·3741	—	0·3251
p-Dimethyl*cyclo*hexane	0·8849	0·8305	0·6726	0·5559	0·4704	0·4094	—	0·3508
n-Propyl*cyclo*hexane	1·277	1·080	0·8606	0·7103	0·5784	0·5019	—	0·4312
n-Butyl*cyclo*hexane	1·714	1·417	1·105	0·8833	0·7249	0·6156	—	0·5222

TABLE XXII.

Data of Mikeska.

(Viscosities in centistokes.)

Hydrocarbon.	T.	v.	T.	v.	T.	v.	T.	v.	T.	v.
Octadecyl*cyclo*hexane (1)	—	—	54·4	8·19	64·2	6·48	77·8	4·87	98·9	3·39
(1-Butyloctadecyl)-*cyclo*hexane (12)	37·8	19·60	54·4	11·45	64·2	8·68	78·3	6·18	98·9	4·17
Docosyl*cyclo*hexane (13)	—	—	54·4	11·93	64·4	9·25	—	—	98·9	4·70
(1-Butylkococyl)*cyclo*hexane (14)	—	—	—	—	64·0	12·14	79·4	8·33	98·9	5·60

Note.—Numbers following names of hydrocarbons refer to those in Mikeska's paper.

PART VI (*a*).

THE VISCOSITIES OF THE ACYCLIC OLEFINES.

Unsaturated hydrocarbons are notoriously difficult to prepare in a state of purity, and to this fact is probably due the small amount of reliable information available on the viscosities of these compounds.

Thorpe and Rodger (*loc. cit.*) made measurements on isoprene, trimethylethylene and di*iso*propenyl (diallyl) over a considerable temperature range, and Ubbelohde and Agthe give results which are practically coincident, and are probably quoted from Thorpe and Rodger's results. Gartenmeister [39] gives a figure at 20° in good agreement with Thorpe and Rodger, whilst Chavanne and van Risseghem (*loc. cit.*) made measurements on one of the heptenes—1 : 2 : 2-trimethylbutene-1—from 0° to 30°. Two acetylene derivatives—*n*-hexylacetylene and nonylacetylene—are represented by single measurements at 25° by Walden and Swinne.[40] Dover and Hensley (*loc. cit.*) have recorded three measurements on octadecene-1, but these are subject to the same criticisms as their data on *n*-octadecane.

We have examined three olefines, none of which has previously been the subject of viscosity measurements—namely, di*iso*butylene, *n*-dodecene-1 and cetene (*n*-hexadecene-1). The di*iso*butylene is, as explained under the preparation of this substance, a mixture of two isomers of slightly different constitution and properties. Landa and his collaborators (*loc.*

TABLE XXIII.

Viscosities of the Monocyclic Naphthenes.

Hydrocarbon.	Empirical Formula.	Mol. Wt.	Viscosity in cp. at					Source of Data.
			0° C.	20° C.	50° C.	80° C.	100° C.	
*cyclo*Pentane	C_5H_{10}	70	0·556	0·4375	0·3245	(0·2525)	(0·2190)	Author.
Methyl*cyclo*pentane	C_6H_{12}	84	0·647	0·501	0·3615	0·274	(0·2345)	
Ethyl*cyclo*pentane	C_7H_{14}	98	0·7415	0·569	0·411	0·3125	0·2685	
1 : 3-Dimethyl*cyclo*pentane	C_7H_{14}	98	0·622	0·508	0·3665	0·2785	0·2380	
n-Propyl*cyclo*pentane	C_8H_{16}	112	0·9035	0·6935	0·491	0·3665	0·312	
n-Butyl*cyclo*pentane	C_9H_{18}	126	1·202	0·8915	0·6095	0·4455	0·3715	
*cyclo*Hexane	C_6H_{12}	84	1·455	0·9865	0·6095	0·413	0·332	
Methyl*cyclo*hexane	C_7H_{14}	98	0·991	0·728	0·4945	0·3665	0·3095	
Ethyl*cyclo*hexane	C_8H_{16}	112	1·161	0·8375	0·5715	0·417	0·350	
o-Dimethyl*cyclo*hexane	C_8H_{16}	112	1·321	0·942	0·625	0·4465	0·369	
m-Dimethyl*cyclo*hexane	C_8H_{16}	112	0·912	0·6855	0·4795	0·3555	0·299	
p-Dimethyl*cyclo*hexane	C_8H_{16}	112	1·081	0·776	0·527	0·3855	0·3245	
n-Propyl*cyclo*hexane	C_9H_{18}	126	1·403	0·993	0·6605	0·4755	0·3945	
1 : 3 : 5-Trimethyl*cyclo*hexane	C_9H_{18}	126	0·891	0·676	0·474	0·354	0·3005	Ubbelohde and Agthe.
n-Butyl*cyclo*hexane	$C_{10}H_{20}$	140	1·910	1·300	0·828	0·5795	0·473	Author.
*iso*Butyl*cyclo*hexane	$C_{10}H_{20}$	140	1·722	1·225	0·7905	0·552	0·4465	Ubbelohde and Agthe.
Cetyl*cyclo*hexane	$C_{22}H_{44}$	292	—	14·95	5·82	3·12	—	Fuel Research Board.
Octadecyl*cyclo*hexane (11)	$C_{24}H_{48}$	336	47·63	19·52	7·467	3·743	2·599	Mikeska.
(1-Butyloctadecyl)*cyclo*hexane (12)	$C_{28}H_{56}$	392	95·50	32·89	10·59	4·838	3·210	
Docosyl*cyclo*hexane (13)	$C_{28}H_{56}$	392	75·48	30·09	11·04	5·355	3·643	
(1-Butyldocosyl)*cyclo*hexane (14)	$C_{32}H_{64}$	448	104·7	47·89	15·05	6·682	4·363	

Note.—Numbers following names of hydrocarbons refer to those in Mikeska's paper.

TABLE XXIV.

Kinematic Viscosities—Monocyclic Naphthenes.

Hydrocarbon.	d^0.	d^{20}.	d^{50}.	0° C.	20° C.	50° C.	80° C.	100° C.
*cyclo*Pentane	0·7621	0·7211	0·6801	0·7295	0·5865	0·4500	0·3625	0·3220
Methyl*cyclo*pentane	0·7676	0·7226	0·6776	0·8430	0·6680	0·5000	0·3940	0·3460
Ethyl*cyclo*pentane	0·7859	0·7449	0·7039	0·9435	0·7395	0·5520	0·4340	0·3815
1 : 3-Dimethyl*cyclo*pentane	0·7639	0·7199	0·6759	0·8145	0·6310	0·5080	0·4015	0·3605
n-Propyl*cyclo*pentane	0·7950	0·7490	0·7030	1·163	0·8940	0·6555	0·5080	0·4440
n-Butyl*cyclo*pentane	0·8003	0·7613	0·7223	1·502	1·136	0·8005	0·6040	0·5145
*cyclo*Hexane	0·7966	0·7506	0·7046	1·827	1·268	0·8120	0·5715	0·4710
Methyl*cyclo*hexane	0·7860	0·7447	0·7034	1·261	0·9460	0·6640	0·5095	0·4400
Ethyl*cyclo*hexane	0·8044	0·7621	0·7198	1·443	1·064	0·7500	0·5660	0·4865
o-Dimethyl*cyclo*hexane	0·8031	0·7638	0·7245	1·644	1·196	0·8185	0·6035	0·5095
m-Dimethyl*cyclo*hexane	0·7882	0·7485	0·7088	1·157	0·8875	0·6405	0·4905	0·4220
p-Dimethyl*cyclo*hexane	0·7887	0·7487	0·7087	1·371	1·004	0·7040	0·5320	0·4580
n-Propyl*cyclo*hexane	0·8078	0·7705	0·7332	1·737	1·252	0·8570	0·6355	0·5380
1 : 3 : 5-Trimethyl*cyclo*hexane	0·7880	0·7505	0·7130	1·131	0·8745	0·6315	0·4865	0·4215
n-Butyl*cyclo*hexane	0·8151	0·7787	0·7423	2·343	1·624	1·063	0·7660	0·6370
*iso*Butyl*cyclo*hexane	0·8102	0·7737	0·7372	2·125	1·540	1·022	0·7340	0·6055
	20° C.		80° C.					
Cetyl*cyclo*hexane	0·8287	0·8086	0·7885	—	18·04	7·197	3·958	—
Octadecyl*cyclo*hexane (11)	0·8431	0·8118	0·7805	56·5	23·5	9·2	4·72	3·33
(1-Butyloctadecyl)*cyclo*hexane (12)	0·8450	0·8146	0·7830	113·0	39·5	13·0	6·08	4·10
Docosyl*cyclo*hexane (13)	0·8479	0·8174	0·7869	89·0	36·0	13·5	6·7	4·63
(1-Butyldocosyl)*cyclo*hexane (14)	0·8518	0·8225	0·7932	123·0	57·0	18·3	8·3	5·5

cit.) have made comprehensive measurements on seven olefines and dienes with from fourteen to twenty-four carbon atoms, while Lerer (*loc. cit.*) has prepared and measured two very viscous compounds with twenty-four and thirty-two carbon atoms, respectively. All these data are recorded in Tables XXV–XXVIII. Table XXIX contains the kinematic viscosity and density data.

Following are the details of preparation and properties of the olefines which have been experimentally examined here.

*Diiso**butylene*.—This substance is a mixture of two isomeric trimethylpentenes, and is obtained by the polymerization of *iso*butylene from cracking gases and subsequent fractionation. A sample of hydrocarbon from this process was refluxed for many hours over metallic sodium to remove non-hydrocarbon impurities, and then refractionated several times. The product obtained had the following properties: b. pt. (corr.), 102·0–102·3° C.; d_4^{20}, 0·7163; d_4^{20}, 0·6913; n_D^{20}, 1·4108; n_D^{25}, 1·4082. Until comparatively recently di*iso*butylene had been considered as a single hydrocarbon, but Whitmore and his collaborators,[41] by means of a very careful fractionation, have shown that it is really a mixture of two isomers with the following properties:

	B. Pt.	d_4^{20}.	n_D^{20}.
2 : 4 : 4-Trimethylpentene-1	101·2° C.	0·7151	1·4082
2 : 4 : 4-Trimethylpentene-2	104·5° C.	0·7211	1·4158

From a comparison of these properties, it appears that the material prepared above contains about 75 per cent. of the lower-boiling isomer and 25 per cent. of the higher.

n-*Dodecene*-1.—The starting point in this preparation was the technical product known as "lorol," prepared by the hydrogenation of coconut oil

or the free fatty acids from coconut oil. It consists of about 60 per cent. of lauryl (dodecyl) alcohol, the remainder being composed of the even-numbered fatty alcohols from C_6 to C_{18}.[42] This material was fractionated, and the fraction boiling at about 125–145° C. at 15 mm. was collected. The crude lauryl alcohol was then distilled with zinc chloride and a mixture of olefines boiling from 140° C. to 220° C. resulted. This mixture was systematically fractionated four times and the best fraction refluxed over sodium and finally distilled. The yield of pure dodecene was not very large, 200 gms. of lorol yielding only about 25 gms. of the purified olefine. The properties of the compound were as follows : b. pt. (corr.), 213 ± 1° C.; d_4^{20}, 0·7600; d_4^{30}, 0·7384; n_D^{15}, 1·4360; n_D^{20}, 1·4338. There is very little data in the literature for comparison of the physical properties, but the figures given in Beilstein and the Int. Crit. Tables indicate that the sample obtained was at least reasonably pure.

TABLE XXV.

Thorpe and Rodger.		Ubbelohde and Agthe.		Thorpe and Rodger.		Ubbelohde and Agthe.		Thorpe and Rodger.		Ubbelohde and Agthe.		Landa and			
												Kejvan.		Riedl.	
*iso*Prene.		*iso*Prene.		Trimethyl-ethylene.		*iso*-Amylene.		Di*iso*propenyl.		Diallyl.		2 : 11-Dimethyldodecadiene.		2-Methylheptadecene-2.	
T.	η.	T.	η.	T.	η.	T.	η.	T.	η.	T.	η.	T.	η.	T.	η.
0·35	0·2589	0	0·2598	0·29	0·2529	0	0·2534	0·37	0·3374	0	0·3390	0	3·095	0	7·1433
5·62	0·2459	10	0·2362	5·64	0·2406	10	0·2310	5·95	0·3169	10	0·3035	10	2·240	10	5·1196
10·27	0·2358	20	0·2154	10·21	0·2306	20	0·2115	10·78	0·3010	20	0·2740	20	1·727	20	3·8368
15·33	0·2249	30	0·1974	15·82	0·2192	30	0·1941	15·46	0·2866	30	0·2491	30	1·418	30	2·9416
20·41	0·2147	40	—	20·03	0·2114			20·76	0·2719	40	0·2272	40	1·195	40	2·3420
25·25	0·2060	50	—	25·75	0·2015			25·46	0·2599	50	0·2076	50	1·019	50	1·8949
28·94	0·1996			30·69	0·1931			30·71	0·2474	60		60	0·894	60	1·5712
32·02	0·1944			32·59	0·1903			36·06	0·2355			70	0·785	70	1·3062
29·93	0·1985							41·99	0·2229			80	0·700	80	1·1354
								46·76	0·2137			90	0·626	90	0·9872
								51·54	0·2047			99	0·558	100	0·8804
								56·20	0·1966						

Landa and										Lerer.			
Habada.		Sliva.		Kejvan.		Riedl.		Čech and Sliva.		Čech and Sliva.			
Diethyl-3 : 12-tetradecenediene-2, 12.		3-Ethyloctadecene-2.		2 : 19-Dimethyleicosadiene.		2-Methyltricosene-2.		4-Propylnonadecane-3.		5-Butyleicosene-4.		Tricaprylene.		7-Methyl-8-β-octyltetracosylene-(7, 8) and (8, 9).	
T.	η.	T.	η.	T.	η.	T.	η.	T.	η.	T.	η.	T.	η.	T.	η.
0	7·218	0	10·540	0	—	0	—	0	17·158	0	24·629	20	25·9	24	17·6
10	5·520	10	7·308	10	5·438	10	—	10	11·650	10	15·981	30	17·4	37	10·7
20	3·987	20	5·324	20	3·972	20	—	20	8·248	20	10·938	40	11·5	61	5·1
30	3·128	30	3·992	30	3·015	30	—	30	6·130	30	8·008	50	9·0	81	3·0
40	2·522	40	3·105	40	2·372	40	—	40	4·717	40	6·032	60	6·4		
50	2·161	50	2·535	50	1·920	50	5·3031	50	3·738	50	4·708				
60	1·822	60	2·035	60	1·576	60	3·967	60	3·337	60	3·742				
70	1·564	70	1·730	70	1·318	70	3·119	70	2·521	70	3·059				
80	1·362	80	1·475	80	1·124	80	2·485	80	2·130	80	2·543				
90	1·212	90	1·263	90	0·972	90	2·047	90	1·730	90	2·174				
99	1·100	99	1·095	99	0·871	100	1·712	99	1·598	99	1·890				

Cetene (n-*Hexadecene*-1).—This hydrocarbon is obtained by the distillation of spermaceti, and is used as a reference fuel in the evaluation of diesel fuels. A sample of material from this source was purified by repeated fractionation *in vacuo*. The quality of the original material being quite good, this treatment was sufficient to produce a pure hydrocarbon. A very pure specimen of cetene was prepared by Waterman,[43] and the constants obtained on this are compared with those of our own sample.

	Our Sample.	Waterman.
B. pt. (corr.) ° C. . . .	158 ± 1°/11½ mm.	157·5°/15½ mm.
d_4^{20}	0·7827	0·7825
d_4^{60}	0·7615	—
n_D^{20}	1·4418	1·4419
n_D^{20}	1·4396	—
A. pt.	72·4° C.	—

TABLE XXVI.

Hydrocarbon.	0° C.	15° C.	20° C.	25° C.	30° C.	Author.
2:2:3-Trimethylbutene-3 .	0·627	0·509	0·480	0·445	0·421	Chavanne and van Risseghem
n-Hexylacetylene . . .	—	—	—	0·657	—	Walden and Swinne
Nonylacetylene . . .	—	—	—	2·00	—	Walden and Swinne
Diisopropenyl . . .	—	—	0·2733	—	—	Gartenmeister

TABLE XXVII.

Hydrocarbon.	5° C.	15° C.	30° C.	45° C.	60° C.	75° C.	80° C.	100° C.
Diisobutylene . .	0·6501	0·5701	0·4745	0·4006	0·3428	0·2972	—	0·2596
n-Dodecene-1 . .	1·803	1·477	1·140	0·9099	0·7463	0·6240	—	0·5311
n-Hexadecene-1 . .	4·677	3·578	2·556	1·887	1·464	1·170	—	0·9511

PART VI (*b*).

THE VISCOSITIES OF THE CYCLIC OLEFINES.

This group of hydrocarbons has received very little attention, the only previously reported data being those of Godchot and Cauquil.[44] These authors examined eleven compounds of the *cyclo*pentene, *cyclo*hexene, *cyclo*heptene and *cyclo*-octene series at a temperature of 13·5° C. The only comparison which can be made with these results is with a value for *cyclo*hexene at 13·5° C., deduced from our own measurements on *cyclo*hexene, which cover the range from 5° C. to 75° C. This value, about 0·716, differs by about 3 per cent. from Godchot and Cauquil's figure. We have not been able to find any other data in the literature on this class of hydrocarbon, so that very little discussion is possible (Tables XXX and XXXI). Tables XXXII and XXXIII give the viscosities of *cyclo*hexene in centipoises and centistokes respectively.

cyclo*Hexene*.—*cyclo*Hexene was purchased from the British Drug Houses, refractionated, refluxed over sodium and again fractionated. The properties of the product were as follows: B. pt. (corr.), 83·1 ± 0·1° C.;

TABLE XXVIII.

Viscosities of the Acyclic Olefines.

Hydrocarbon.	Empirical Formula.	Mol. Wt.	Viscosity in cp. at 0° C.	20° C.	50° C.	80° C.	100° C.	Source of Data.	Remarks.
Trimethylethylene	C_5H_{10}	70	0·2535	0·211	(0·1665)	(0·138)	(0·124)	Thorpe and Rodger	B. pt. 38·4° C.
Isoprene	C_5H_8	68	0·2605	0·216	(0·171)	(0·141)	(0·125)	Thorpe and Rodger	B. pt. 34·0° C.
Diallyl	C_6H_{10}	82	0·3405	0·273	0·208	(0·166)	(0·145)	Thorpe and Rodger	B. pt. 60·0° C.
2 : 2 : 3-Trimethylbutene-3	C_7H_{14}	98	0·625	0·475	(0·334)	—	—	Chavanne and van Risseghem	
2 : 4 : 4-Trimethylpentene (1 and 2)	C_8H_{16}	112	0·6965	0·5345	0·380	0·2825	0·2365	Author	
n-Dodecene-1	$C_{12}H_{24}$	168	2·004	1·346	0·851	0·589	0·483	Author	
2 : 11-Dimethyldodecadiene	$C_{14}H_{26}$	194	3·095	1·738	1·012	0·695	0·566	Landa and Kejvan	Mainly 2 : 11-dimethyldodecadiene-1, 11
n-Hexadecene-1	$C_{16}H_{32}$	224	5·408	3·177	1·718	1·096	0·871	Author	
2-Methylheptadecene-2	$C_{18}H_{36}$	252	7·143	3·837	1·875	1·127	0·875	Landa and Riedl	
3 : 12-Diethyltetradecanediene-2, 12	$C_{18}H_{34}$	250	7·218	3·987	2·125	1·368	1·090	Landa and Habada	
3-Ethyloctadecene-2	$C_{20}H_{40}$	280	10·54	5·272	2·535	1·466	1·086	Landa and Sliva	
2 : 19-Dimethyleicosadiene	$C_{22}H_{42}$	306	7·834	3·972	1·905	1·122	0·851	Landa and Kejvan	Mixture of at least two isomers
4-Propylnonadecene-3	$C_{22}H_{44}$	308	17·16	8·248	3·738	2·100	1·575	Landa, Čech and Sliva	
2-Methyltricosene-2	$C_{24}H_{48}$	336	—	(16·90)	5·303	2·485	1·726	Landa and Riedl	M. pt. 41·5° C.
4-Butyleicosene-4	$C_{24}H_{48}$	336	24·63	10·94	4·708	2·543	1·855	Landa, Čech and Sliva	
Tricaprylene	$C_{24}H_{48}$	336	—	25·94	8·67	3·90	—	Lerer	
7-Methyl-8-β-octyltetracosylene (7, 8 and 8, 9)	$C_{33}H_{64}$	448	(55·46)	20·99	7·015	3·069	(1·950)	Lerer	

TABLE XXIX.

Kinematic Viscosities—Acyclic Olefines.

Hydrocarbon.	d_4^0.	d_4^{50}.	d_4^{100}.	Viscosity in cs. at				
				0° C.	20° C.	50° C.	80° C.	100° C.
Trimethylethylene	0·6850	0·6365	—	0·3701	0·3171	0·2616	—	—
Isoprene	0·6912	0·6437	—	0·3769	0·3219	0·2657	—	—
Diallyl	0·7074	0·6580	—	0·4814	0·3971	0·3161	0·2640	—
2:2:3-Trimethylbutene-3	0·7235	0·6793	—	0·8640	0·7630	0·4916	—	—
2:2:4-Trimethylpentene (1 and 2)	0·7330	0·6913	0·6496	0·9501	0·7461	0·5496	0·4239	0·3641
n-Dodecene-1	0·7744	0·7384	0·7024	0·587	1·771	1·153	0·8217	0·6877
2:11-Dimethyldodecadiene	0·8220	0·7869	0·7509	3·765	2·155	1·286	0·9080	0·7537
n-Hexadecene-1	0·7968	0·7615	0·7262	6·787	4·060	2·256	1·480	1·199
2-Methylheptadecene-2	0·8089	0·7761	0·7449	8·831	4·823	2·415	1·486	1·174
3:12-Diethyltetradecanediene-2, 12	0·8249	0·7929	0·7609	8·752	4·909	2·681	1·768	1·433
3-Ethyloctadecene-2	0·8181	0·7844	0·7511	12·88	6·557	3·232	1·919	1·445
2:19-Dimethyleicosadienes	0·8311	0·7976	0·7630	9·426	4·857	2·389	1·445	1·115
4-Propylnonadecene-3	0·8182	0·7858	0·7512	20·97	10·25	4·756	2·745	2·097
2-Methyltricosene-2	0·8334	0·7994	0·7656	—	20·61	6·634	3·190	2·254
5-Butyleicosene-4	0·8205	0·7889	0·7566	30·01	13·54	5·968	3·306	2·452
Tricaprylene	0·8505	0·8175	0·7845	—	30·98	10·60	4·889	—
7-Methyl-8-β-octyltetracosylene (7, 8 and 8, 9)	0·8604	0·8206	0·7876	64·46	24·77	8·549	3·832	2·476

d_4^{20}, 0·8104; d_4^{20}, 0·7823; n_D^{20}, 1·4469; n_D^{25}, 1·4445. Waterman and Van Westen [45] obtained 82·8°/759 mm. for the boiling point and 1·4464 for n_D^{20}.

TABLE XXX.

Hydrocarbon.	Viscosity at 13·5° C.
*cyclo*Pentane	0·429
1-Methyl*cyclo*pentene-1	0·442
*cyclo*Hexene	0·696
1-Methyl*cyclo*hexene-1	0·737
1-Methyl*cyclo*hexene-3	0·726
1:4-Dimethyl*cyclo*hexene-1	0·716
1:3:4-Trimethyl*cyclo*hexene-3 or -4	0·884
*cyclo*Heptene	1·240
1-Methyl*cyclo*heptene-1	1·079
cyclo-Octane	1·801
1-Methyloctane-1	4·879

TABLE XXXI.

Hydrocarbon.	5° C.	15° C.	30° C.	45° C.	60° C.	75° C.	90° C.
*cyclo*Hexene	0·8072	0·7001	0·5806	0·4811	0·4069	0·3515	—

TABLE XXXII.

Viscosities of the Cyclic Olefines.

Hydrocarbon.	Empirical Formula.	Mol. Wt.	Viscosity in cp. at					Source of Data.	Remarks.
			0° C.	20° C.	50° C.	80° C.	100° C.		
*cyclo*Hexene	C_6H_{12}	82	0·871	0·653	0·455	0·3365	0·2825	Author	B. pt. 83° C.

TABLE XXXIII.

Kinematic Viscosities of the Cyclic Olefines.

Hydrocarbon.	d_4^0.	d_4^{20}.	d_4^{100}.	Viscosity in cs. at				
				0°.	20°.	50°.	80°.	100°.
*cyclo*Hexene .	0·8291	0·7823	0·7355	1·051	0·8058	0·5816	0·4461	0·3841

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CRYSTAL TWINS OF NORMAL $C_{24}H_{50}$ AND THE INFLUENCE OF PHASE TRANSITIONS ON THEIR ORIENTATION.*

By E. C. H. Kolvoort.

Synopsis.

1. Twin structure was studied upon a preparation of $C_{24}H_{50}$. The (110) and (310) planes may act as twinning planes.
2. $C_{24}H_{50}$ is optically positive at room temperature, it is biaxial, $\rho < \nu$. 2 E about 45°.
3. At 41° C. and 46° C. a transition into a different solid phase was observed in pure synthetic n-$C_{24}H_{50}$, setting point 50·8° C. Above 46° C. the crystal was optically uniaxial, with positive bi-refringence, probably hexagonal.
4. Between 41° C. and the melting point the crystals are very soft, between 41 and 46° C. other combinations of twins can be formed on application of lateral pressure.
5. The lower point of transition is more strongly decreased by contaminations than the upper.

Material.

When preparing a number of narrow fractions of a Borneo paraffin wax (melting point 130–135° F.) by distillation with the aid of steam and vacuum in a good fractionating column, it was found on solidification of the fractions obtained that these were coated with a thin film exhibiting little cohesion to the remainder of the paraffin wax. This film could very easily be split into thin plates, like mica. Probably these are paraffin wax crystals formed from molecules originally oriented in a sense perpendicular to the surface of the molten mass. A similar process of growth is presumed by Fuchs,[1] among others, who studied the formation of very thin crystals of $C_{34}H_{70}$ at the surface of solutions in medicinal oil.

Structure.

When examined through the polarizing microscope, every cleavage plate proved to consist of a large number of differently oriented individual crystals, similar to the preparations described by Yannaquis.[2] The largest dimension of these crystals was very seldom more than 1 mm., usually much less. The individuals were found to be arranged in a systematic manner, as could clearly be observed by turning round the preparation on the stage of the polarizing microscope between crossed nicols.

The arrangement can be explained by twinning. The twinning planes have been determined as well as the orientation of the unit cells of the crystals in the various individuals.

It is assumed that cleavage takes place in a sense parallel to (001). This is all the more probable, as long carbon chains, especially with polar end groups, are known to have the tendency to orient in a sense parallel to each other, and perpendicular or at a certain angle to solid or liquid inter-

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faces; it is hence also likely that this has occurred in the case of the material under investigation, which was formed as a skin on the surface of a melt. Moreover, we know that the (001) plane is the most strongly developed plane of the plate-like crystals formed from a solution of normal hydrocarbons in various solvents.

Composition.

The melting point of the material studied was 50·5–50·9° C. (capillary). The refractive index $n_D^{57\cdot5}$ was found to be 1·4225, from which it follows, according to an empirical relation found for normal straight-chain hydrocarbons:

$$n_D^t = n_D^{t'} - (2{\cdot}95 \times 10^{-4} + 1{\cdot}65 \times 10^{-6}\,\theta)\,(t - t')$$

in which:

t = temperature in ° C.

θ = melting point in ° C.

that

$$n_D^{20} = 1{\cdot}4216.$$

A synthetic product n-$C_{24}H_{50}$ of great purity was found to have a setting point of 50·8° C., the refractive index n_D^{60} being 1·4211.

From this it follows that the preparation examined consists, practically, of normal $C_{24}H_{50}$ or a solid solution of this average composition.

Crystallography.

The structure of the space lattice of some normal aliphatic hydrocarbons is known from X-ray analysis, especially from measurements carried out by Müller.[3-8] The spacing perpendicular to the longitudinal direction of the molecules, irrespective of what system the crystals belong to, was found to be "a" = 7·41 and "b" = 4·94 A° for $C_{24}H_{50}$, the angle between two (110) planes amounting to 67° 20′ at 18·7° C. For other normal aliphatic hydrocarbons the length of "a" and "b" is found to be about the same; the spacing perpendicular to the (001) plane for a certain class of crystal symmetry is a linear function of the number of C atoms per molecule.

A normal paraffin wax can crystallize in various crystal classes. Müller describes crystals of $C_{29}H_{60}$ as being orthorhombic.[4] Besides this orthorhombic symmetry, monoclinic and triclinic forms have been described, whilst the hydrocarbons $C_{22}H_{46}$ to $C_{29}H_{60}$ were proved to have a hexagonal arrangement of the molecules in a temperature range just below the melting point.

It was not further ascertained in what system the preparations had crystallized; at room temperature it is most likely, however, that we are concerned with the monoclinic form.

For interpreting the crystallographical measurements the data relating to the orthorhombic modification of $C_{29}H_{60}$ [4] have been used, as with the preparation studied only the angles between the lines of intersection of ($hk0$) planes with the (001) plane have been determined, and it is, moreover, known that at room temperature these angles vary very little with the number of C atoms per molecule.

For $C_{29}H_{60}$ the ratio of the a and b edges of the unit cell is 7·45 : 4·97. The twinning planes observed obviously belong to the $\{hk0\}$ zone. With the aid of these data it is possible to calculate the angles between the possible twinning planes, so that these may then be compared with the angles observed.

The measurements soon showed that the number of different angles in the cleavage plates remained very limited. Thus, the following angles were measured between the lines of intersection of the twinning planes and the (001) plane:

Series I. 31·5, 32·0, 31·4, 28·6, 31·0, 30·0, 29·0, 30·5 or their supplements.

Series II. 83·2, 83·3, 82·0, 83·4, 85·0, 83·0, 81·8 or their supplements.

Besides this, the angles between a line of intersection of a twinning plane with the (001) plane and one of the directions of extinction were measured. In these small individuals, however, the latter could not always be determined with great exactitude, so that considerable spreading was found:

Series III. 35·0, 35·3, 31·8, 36·0, 31·2, 38·0, 36·3, 37·5, 29·7, 36·0, 39·0 or their supplements.

Series IV. 24·8, 26·0, 27·0, 26·0, 26·0, 27·0 or their supplements.

It was further assumed that the directions of extinction correspond to the direction of the a and b axis of the unit cell. With the aid of the known relation between a and b, the angles between the lines of intersection of the planes with simple indices and the (001) plane can be calculated. The results are:

For the angle formed by the lines of intersection of (310) and (110) with (001), the value 29·8°, corresponding to series I.

For the angle formed by the lines of intersection of (310) and (110) with (001), the value 82·8°, corresponding to series II.

For the angle formed by the lines of intersection of (110) and (010) with (001), the value 33·7°, corresponding to series III, and

For the angle formed by the lines of intersection of (310) and (100) with (001), the value 26·5°.

Twinning therefore appears to occur with respect to (110) and (310), the good agreement between calculation and observation confirming the fact that the direction of extinction is parallel to the lines of intersection of (010) or (100) with (001)—*i.e.*, parallel to the a and b axis of the unit cell. In Fig. 1 these lines of intersection of the twinning planes with the (001) plane are given. The shape of the crystal individuals is completely governed by the twinning planes. Some frequent shapes and combinations are given in Fig. 2. The dashed lines indicate the direction of extinction parallel to (010). We are therefore here concerned with parallel extinction, although the peculiar shape of the twin individuals may cause the phenomenon to be interpreted as oblique extinction (Yannaquis).[2] The crystal symmetry is therefore not triclinic, but monoclinic or orthorhombic.

The result of Müller's X-ray investigations may explain the reason of (310) being a twinning plane. For, if the 4 molecules per unit cell are projected on the (001) plane, the result is a pattern as shown in Fig. 3.

This shows that (100), (310), (110) and (010) are the most densely occupied planes. It is possible that (010) and (100) may also occur as twinning

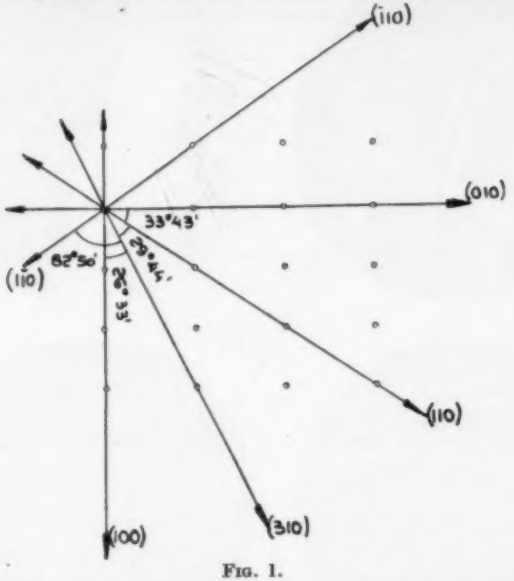


FIG. 1.

PROJECTION OF THE (110) AND (310) TWINNING PLANES ON TO THE (001) PLANE (PLANE OF DRAWING) GIVING THE ANGLES. THE DOTS ARE THE PROJECTED C EDGES OF THE UNIT CELLS.

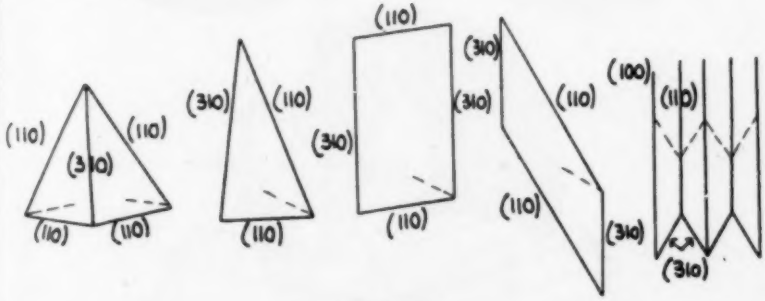


FIG. 2.

SOME OF THE CRYSTAL INDIVIDUALS OBSERVED AND THEIR TWINNING COMBINATIONS. THE DASHED LINES INDICATE THE DIRECTION OF EXTINCTION PARALLEL TO (010).

planes; in the preparations studied this could not, however, be observed optically.

Müller gives the distance m as $\frac{4}{3\bar{1}0}\,a$ (Fig. 3), from which it follows that the distance $n = \frac{11}{3\bar{1}0}\,a$. Should the molecule p be situated in the (310) plane, n should be $\frac{12}{3\bar{1}0}\,a$, which makes a difference of $\frac{1}{3\bar{1}0}\,a = 0{\cdot}25$ A° from the value

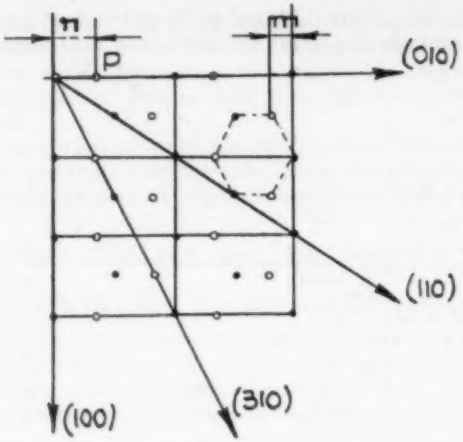


FIG. 3.

PROJECTION PERPENDICULAR TO THE (001) PLANE OF THE (110) AND (310) TWINNING PLANES AND OF THE MOLECULES IN THE UNIT CELLS (ACCORDING TO MÜLLER).

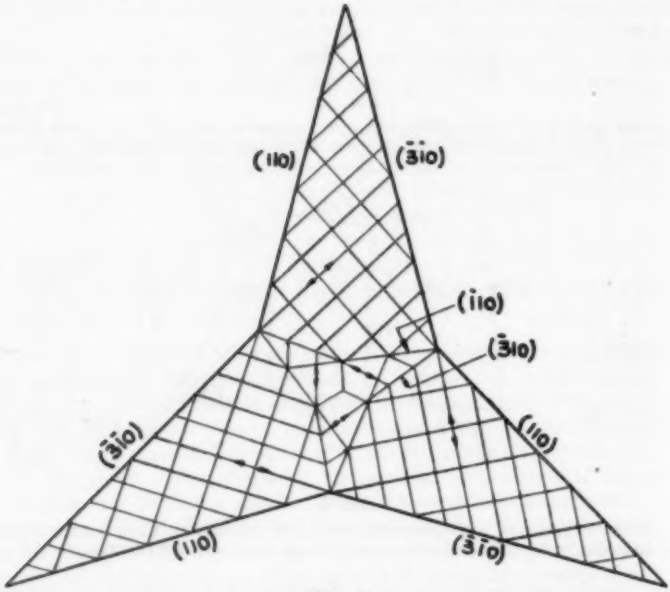
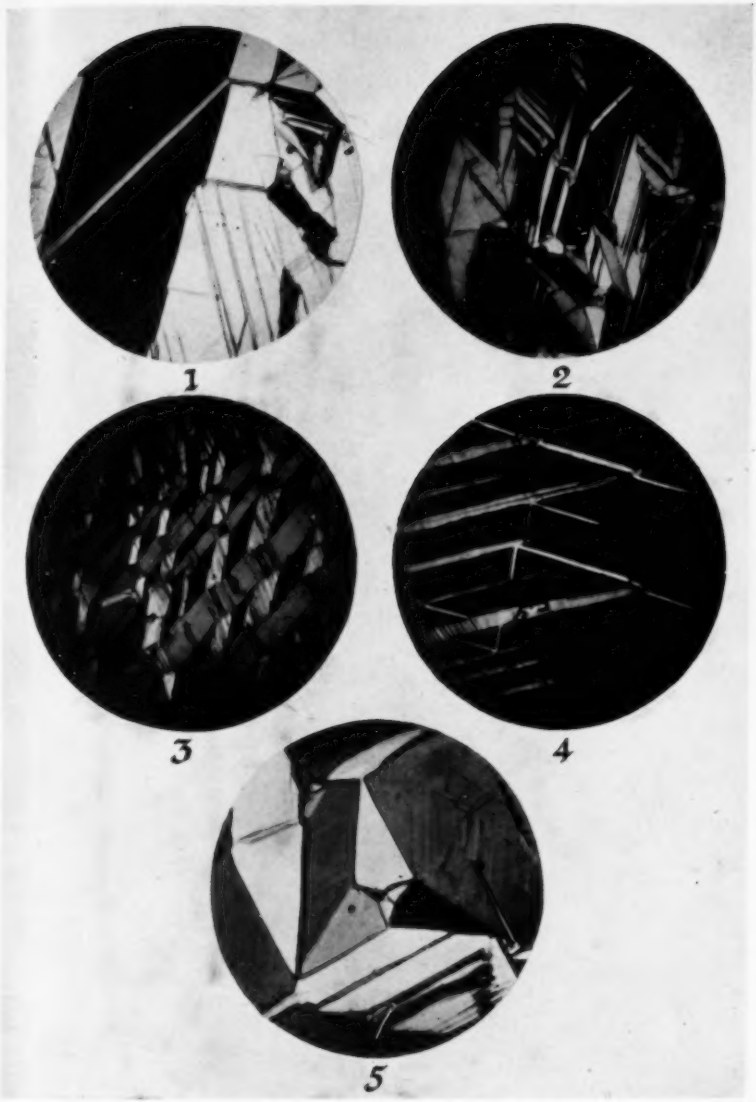


FIG. 4.

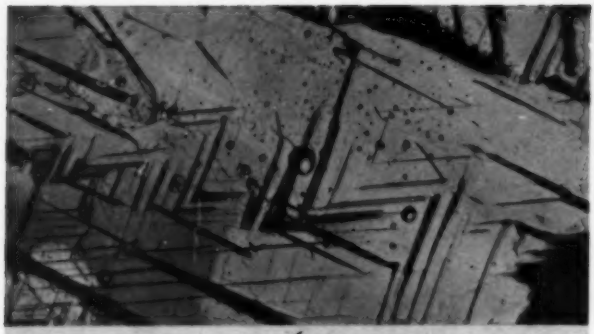
PROJECTION PERPENDICULAR TO THE (001) PLANE OF THE RHOMBIC UNIT CELLS OF A COMBINATION OF CRYSTAL TWINS OF PARAFFIN WAX.

THE RECTANGLES INDICATE THE CROSS-SECTION OF THE UNIT CELLS PERPENDICULAR TO THE MOLECULES, THE ARROWS THE DIRECTION OF EXTINCTION. (CF. PHOTOGRAPH 5.)



1. Twins with respect to (110) and (310).
2. Symmetrically constructed twins with respect to (310).
3. Combination of twins with three different directions of orientation of crystal lattice.
4. Combination of twins with three different directions of orientation of crystal lattice of which one direction dominates strongly over the rest.
5. Twins with respect to (110) and (310) forming a three-pointed star.

[*To face p.* 342.



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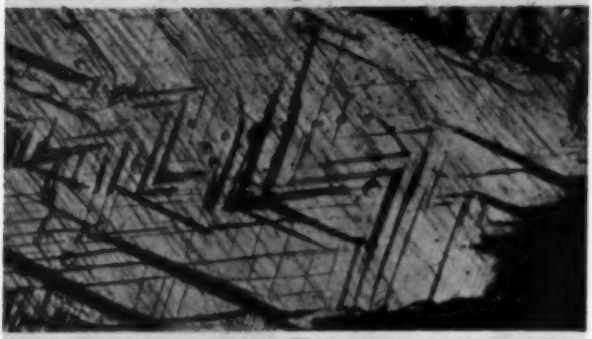

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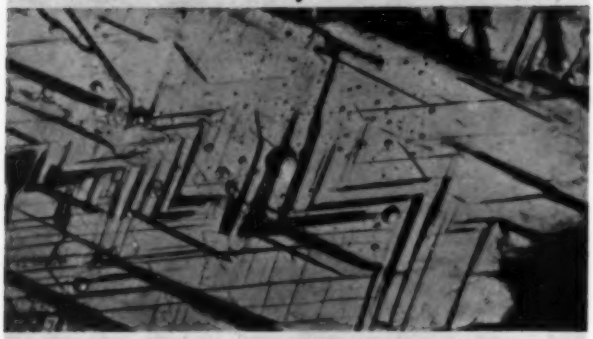

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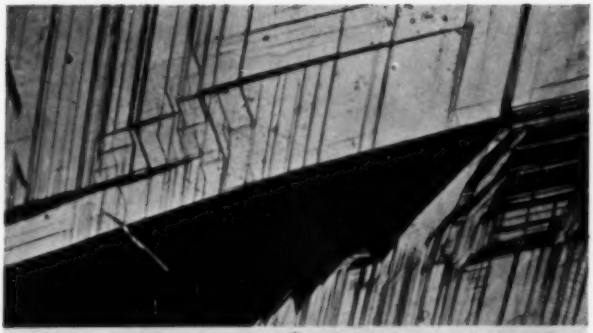
6. Twin structure at 34·6° C. γ Modification.
7. Twin structure at 36·5° C. during the transition from the γ to the β modification.
8. Twin structure at 37·1° C. β modification.



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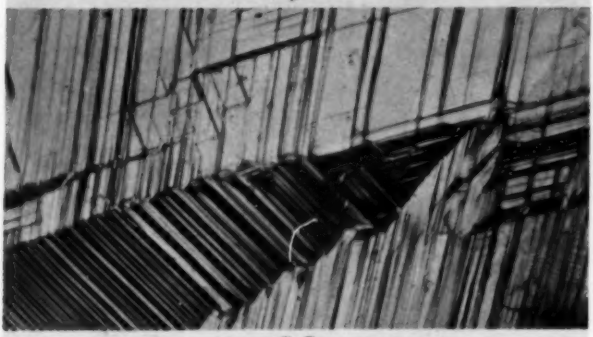

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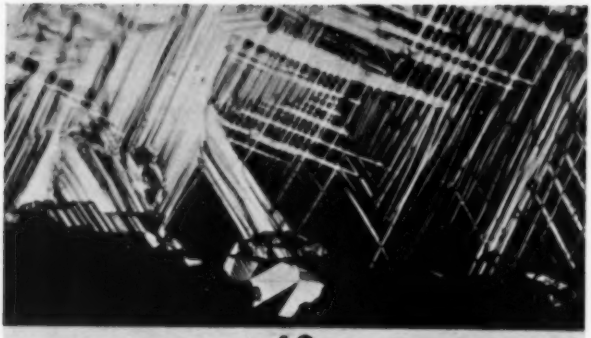
11

9. Paraffin wax. Alteration in the twin structure owing to shearing at 37·2° C.
10. Paraffin wax. Alteration in the twin structure owing to shearing at 37·2° C.
11. Paraffin wax. Alteration in the twin structure owing to shearing at 37·2° C.



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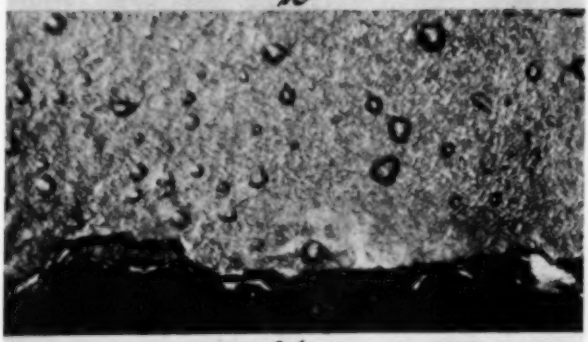
12. Twin structure at 37·2° C. β modification.
13. Twin structure at 44·9° C.; the β modification has almost entirely passed into the α modification.
14. Twin combination after passing into the α modification at 45·1° C.

15



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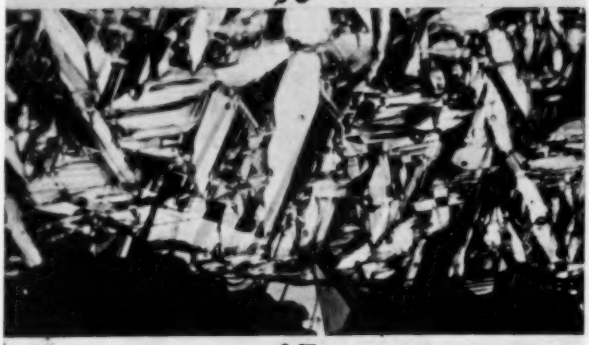

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15. Twin combination in the α modification at 46·4° C. Preparation pressed together.
16. Twin combination in the α modification, about 0·3° C. below the melting point.
17. Twin structure in the β modification at 43·8° C., started from the α modification.

18

19

20

18. Twin structure in the β modification at 38·1° C., started from the α modification.
19. Flat needles formed on cooling of melted pure n-$C_{24}H_{50}$. α modification.
20. Twin structure of pure n-$C_{24}H_{50}$ formed by cooling of the α modification to 44·6° C. β modification.

given. This difference may be ignored, considering the dimensions of the zigzag-shaped molecule, the width of which was found to be 1·6 A°, so that we may safely speak of a dense occupation of the (310) plane.

With the aid of the angles measured, it is possible to indicate the position of the unit cells in the preparations. This was worked out for part of photograph 5. Several times it was observed that the twins happened to orient themselves so as to form a three-pointed star. The *a* and the *b* axes of the unit cells are given in a (001) plane (= plane of projection in Fig. 4). The double-pointed arrows indicate one of the directions of extinction, and are at the same time the projection of the optic axes situated in the (010) plane.

One of the preparations contained a crystal large enough to enable us to measure the angle of the optic axes 2 E directly (Wülfing's method). 2 E was found to be about 44° at room temperature. Reistle and Blade give this as about 45°,[11] and Yannaquis [2] mentions 42–48°, with strong variations. The angle between the optic axes is smaller for red light than for blue. The sign of bi-refringence is positive.

Behaviour of the Crystals When the Temperature Changes.

Transitions between Different Modifications.

The preparations behaved in a remarkable way when subjected to heating or cooling. Between 20° C. and the melting point two marked transition points were found at 36° C. and 45° C. For the sake of convenience the modification between the melting point and 45° C. will be referred to as the α form, that between 45° and 36° C. as the β form, and that below 36° C. as the γ form.

No change of the twin structure occurs as a consequence of the transition from $\beta \underset{\longleftarrow}{\overset{36°}{\rightarrow}} \gamma$. During this transition the surface of the preparation exhibits many wrinkles parallel to the *b* axis of the unit cell. This phenomenon could be repeated any number of times by heating and cooling the preparation, and was reproducible to within some tenths of a degree. Photograph 6 shows the appearance at 34·6° C. of the γ form, photograph 7 was taken during the transition from the γ into the β form at 36·5° C., whilst photograph 8, taken at 37·1° C., shows the β form. The structure has remained the same, the colour of the preparation was slightly more yellow below the temperature of transition than above it. This was observed with several preparations, and points to stronger bi-refringence of the γ modification.

Perhaps we are here concerned with a monoclinic γ form, which passes into an orthorhombic β form, retaining the orientation of the molecules with respect to each other in the (001) plane. We must then imagine that the originally tilted molecules (γ form) take up a position perpendicular to the (001) plane, without any rotation of the zigzag-shaped molecules about their longitudinal axes.

A dilatometric investigation showed that the specific volume strongly increased during the transition from the γ to the β form, whereas the transition from the β form into the α form took place without any appreciable increase or decrease of the specific volume.

The β form was markedly soft, unlike the γ form. By shifting the glasses between which the preparation was held, with respect to each other, it was possible in the β form to convert the twin structure into various other twin combinations (photographs 9, 10, 11). If too much pressure was exerted on the preparation, the vertical orientation of the molecules was disturbed and the preparation lightened considerably at that spot, because of the much higher bi-refringence in a direction perpendicular to the *c* axis of the unit cell (see photograph 15, which shows this in the case of the α form).

If the β form was further heated, the contrasts in light intensity between the differently oriented individuals became less marked and suddenly disappeared altogether at 45° C. This is shown in photographs 12, 13 and 14. Photograph 12 shows the β form at 37·2° C. Especially the thin part along the edge clearly shows the twin structure. Photograph 13 was taken at 44·9° C. The fragment of crystal at the end is already dark. The other part still consists of a mixture of the β and the α forms. Photograph 14 illustrates the preparation at 45·1° C. after it has almost completely passed into the α form. In this form the crystal no longer shows bi-refringence in the direction perpendicular to the cleavage plane. By shifting the glasses between which the crystal plate is placed, the molecules can here also be brought out of their vertical position, which causes a considerable lightening up of the disarranged parts of the crystals (photograph 15). Apparently the α form is uniaxial. If the α form is cooled, a twin structure is suddenly formed at 45° C., deviating from that which existed before it was heated (photograph 17). Further cooling emphasizes the contrasts, but does not alter the structure any more (photograph 18).

The alteration of the structure of the crystal was also studied by observing the alteration of the interference figure obtained from a crystal individual placed at an angle of 45° to the direction of vibration of the polarized light in the nicols. In the γ form the angle of the optical axes is only slightly dependent on the temperature; if the temperature rises, it decreases slightly. During the transition to the β form the angle between the optical axes decreases within some tenths of a degree Centigrade by about 20 per cent. of the value of the γ form. After that the axial angle greatly depends on the temperature up to the point of transition from $\beta \xrightarrow{45° C.} \alpha$, at which point the interference figure for uniaxial crystals is formed. The crystal now remains uniaxial with positive bi-refringence up to the melting point.

If the α form is further heated, it falls apart at about 0·3 C. below the melting point into innumerable plate-shaped fragments of crystal, which, as soon as they are no longer exactly horizontal, become considerably lighter as a result of strong double refraction owing to the fact that the rays of light form an angle to the optical axis of the crystals (see photograph 16). At the edge of the preparation incipient melting is clearly perceptible. Piper [19] describes a similar phenomenon as a point of transition some tenths of a degree Centigrade below the melting point, which is only visibly perceptible, but cannot be detected by X-ray analysis.

The phenomena observed were repeated in a pure, synthetic preparation of $C_{24}H_{50}$. When the preparation was allowed to cool after melting, broad needles and plates of the α form were first formed (photograph 19); these passed into the β form at 46° C. On plates situated in a favourable position the development of a twin structure could be observed (photograph 20).

The second transition point was at 41° C.—*i.e.* 5° higher than in the case of the impure preparation described above.

The temperatures of transition in ° C. were found to be :

Impure preparation : melting point 50·5–50·9° C.

$$\begin{array}{l} 44{\cdot}5\text{–}44{\cdot}6 \downarrow \overset{\alpha}{\underset{\beta}{\underset{\gamma}{\uparrow}}} \uparrow 44{\cdot}9\text{–}45{\cdot}1 \\ 36{\cdot}0\text{–}36{\cdot}2 \downarrow \qquad\quad \uparrow 36{\cdot}5\text{–}36{\cdot}7 \end{array}$$

Pure preparation : melting point 50·8° C.

$$\begin{array}{l} 45{\cdot}8;\ 46{\cdot}0;\ 46{\cdot}1 \downarrow \overset{\alpha}{\underset{\beta}{\underset{\gamma}{\uparrow}}} \uparrow 46{\cdot}4;\ 46{\cdot}4 \\ 40{\cdot}6 \qquad\quad \downarrow \qquad\quad \uparrow 41\text{–}43 \end{array}$$

During the transition in the pure preparation from the β form to the γ form, however, the twin structure was completely disturbed, which did not happen in the preparations described above. Perhaps the twins formed still contain too many disturbances in the β form. The temperatures found may, however, be compared with the data obtained by X-ray analysis by Müller [7] for $C_{24}H_{50}$. It is seen that the transition from γ to β corresponds to the sudden displacement of the (200) reflection. Beyond that point the structure approximates more and more to that of the hexagonal system (Fig. 5). The point at which the pseudo-hexagonal orthorhombic system passes into the hexagonal system (α form) was not detected by X-ray analysis. This transition may be clearly observed microscopically, however, and occurs suddenly at 46° C. probably at the same temperature as that at which all the molecules rotate, consequently assuming radial symmetry.[14]

The fact that the contrasts in the β form become less definite when the temperature rises may be associated with an increasing oscillation of the molecules. Cooling of the α form makes rotation cease at a given moment, and the molecules prove to form an orthorhombic twin structure.

Measurements carried out by Mazee [13] showed that the transition from α to β is accompanied by a great heat effect. For pure *n*-$C_{24}H_{50}$ 21·0 cal./gm. was found at 47·4° C.; the heat of fusion at 50·8° C. was 60·8 cal./gm.

Yannaquis [2] describes a point of transition at 36·5–37·2° C. for a distillate fraction with a melting point of 49·0–49·5° C. The phenomena observed exactly resemble those observed with our preparation at 46° C. Apparently, therefore, the transition from α to β has occurred here, at some lower temperature than was to be expected, considering the melting point, owing to the fact that no highly pure product had been used.

In a previous article,[12] Yannaquis, referring to impure paraffins, describes this phenomenon as being a direct transition from the hexagonal system into an orthorhombic system, whereas with pure paraffins the hexagonal form first gradually passes into a second orthorhombic modification before the transition into the other orthorhombic modification takes place. Yannaquis therefore assumed that he was observing the transition point from α to γ, but it may be gathered from the description that it is more likely to have been the transition from α to β. The transition from β to γ, which is even more strongly affected by foreign components, must have occurred considerably lower.

The points of transition described by Piper [10] and other investigators for n-$C_{26}H_{54}$ are situated at 55·5–56·0° C. and 48·3–52° C., at a melting point of 56·4–56·6° C. The former transition point was only observed in a melting-point capillary, but it was not possible to detect it by X-ray analysis. The modification above the lower transition point is indicated as the A form and its spacing perpendicular to the cleavage plane (001) is about 10 per cent.

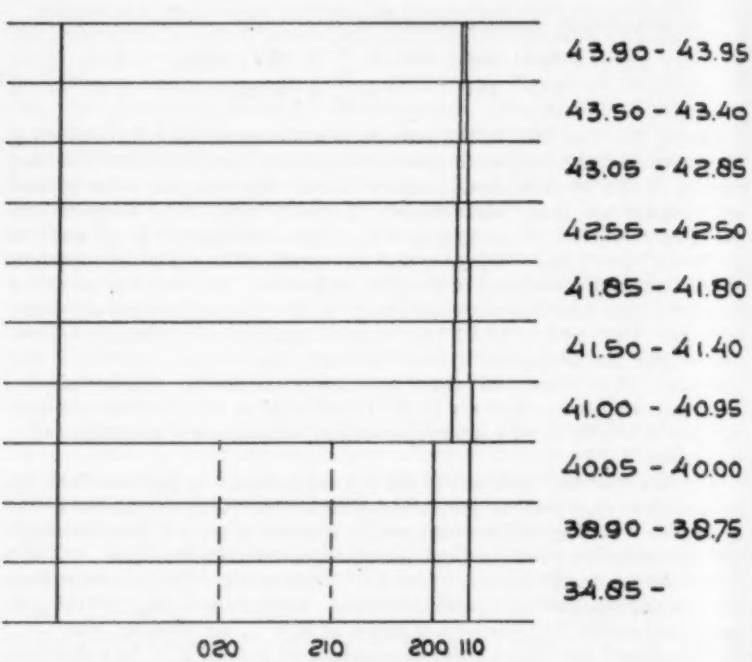


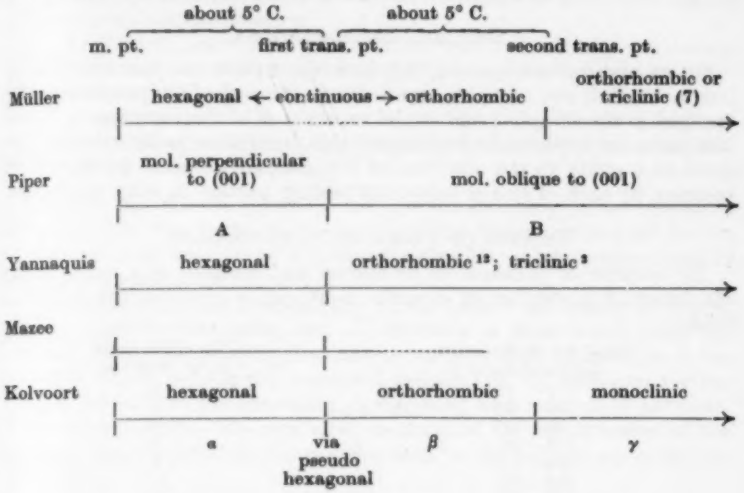
FIG. 5.

REFLECTIONS OF X-RAYS OBTAINED WITH n-$C_{24}H_{50}$ AT SUCCESSIVE TEMPERATURES. (ACCORDING TO MÜLLER.)

larger than in the C form below this transition point. At normal temperatures paraffin waxes with an odd number of C atoms less than 11 and an even number of C atoms less than 26 would occur in a B form, with a spacing between that of the C and A forms. The C form occurs only with waxes with an even number of C atoms larger than 24. In the A form the molecules are considered to be perpendicular to the cleavage plane, in the B and C forms they are oblique to it. It is possible that the A form corresponds to the hexagonal α form described in the present publication, and the B form (or C form) to the γ form. The temperature at which the X-ray photographs were taken of the B and C forms is not given. If this temperature is lower than the transition point from β to γ, this explains why the β

form was not identified. The spacing in this orthorhombic β modification ought to be equal to that of the hexagonal form.

As regards the points of transition of n-$C_{24}H_{50}$ or of paraffin-wax fractions with approximately this composition (Yannaquis), the following comparative diagram may be drawn up :



ACKNOWLEDGEMENT.

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STANDARD METHOD (TENTATIVE) FOR SAMPLING ASPHALTIC BITUMEN IN PACKAGES.

I.P.T. Serial Designation—S.3 (T).

General Considerations.

No set of directions for sampling, however explicit, can take the place of judgment, skill and previous experience on the part of the person actually engaged in the sampling and in the supervision of the sampling. These directions are intended to supplement this experience, and particularly to serve as a guide to the selection of the method which is to be used in common by each of two or more contracting parties in cases of dispute.

Number of Packages to be Sampled.

The number of packages to be opened and sampled in a consignment consisting of a number of separate packages is given in the following table :—

Total No. of Packages in Consignment	No. of Packages to be Sampled.
1– 25	3
26– 50	4
51– 100	5
101– 200	6
201– 300	8
301– 400	10
401– 500	12
501–1000	17

When the total number of packages in the consignment exceeds 1000, the number of packages to be sampled shall be 17 plus 1 per cent. of the number in excess of 1000.

Method of Taking Sample.

For solid or semi-solid products, samples shall be taken at least 3 in. below the surface, and at least 3 in. from the side of the package. A hammer and chisel may be used if the material is hard enough to be chipped out, and a broad, stiff putty-knife if the material is soft. For liquid products, samples shall be taken by the methods prescribed under paragraph 44 (" Sampling Petroleum and Petroleum Products " (I.P.T. Serial Designation S.1)).*

The weight of each individual sample taken shall be *not less* than 2 lb.

Treatment of Samples.

Each sample shall be submitted to the appropriate specification test—viz., penetration, viscosity or melting point.

The question of carrying out further specification tests on individual samples or on a bulked sample shall be left to the discretion of the purchaser.

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* *Standard Methods for Testing Petroleum and its Products*, Third Edtion, 1935, p. 10.

Basis of Acceptance or Rejection.

The consignment shall be rejected if any one sample shall be outside the specification limits to the extent set out hereunder :

25 per cent. above the upper, or 25 per cent. below the lower penetration specification limits for asphaltic bitumens purchased against a penetration specification.

25 per cent. above the upper, or 25 per cent. below the lower viscosity specification limits for cutback asphaltic bitumens and road oils purchased against a viscosity specification.

10 per cent. above the upper, or 10 per cent. below the lower melting-point specification limits for hard asphaltic bitumens purchased against a melting-point specification.

Provided that the consigment is not rejected according to the conditions set out above, the basis of acceptance of the consignment shall be the average result of tests on all the separate samples, which average shall be within the specification limits.

If, in computing the average, any of the results are widely divergent from the specification limits, and the inclusion of these would cause the rejection of the consignment, then further samples shall be drawn from the packages which have given abnormal results and, in addition, further samples taken from the remaining packages up to a total of 15 per cent. of the consignment. The new average obtained by the inclusion of the results of tests on such further samples shall be the basis of acceptance or rejection.

THE APPLICATION OF PHYSICO-CHEMICAL PRINCIPLES TO THE INVESTIGATION OF THE PROPERTIES OF ROCKS.

PART I.

POROSITY—ORIGIN, SIGNIFICANCE AND MEASUREMENT.*

By A. H. Nissan, B.Sc. (Student).

Synopsis.

This paper, although of an introductory character, summarizes the theories and methods employed in the investigation of porosity. The origin of macro-porosity in rocks has been considered specifically with reference to the oil industry and the significance of porosity in estimating reservoir capacity has been interpreted. The development of the quantitative study of porosity has been treated chronologically, beginning with Melcher's gravimetric method (1921) and ending with the Bureau of Mines high pressure air experimental method (1937); in certain cases the sequence of dates has been interrupted. In addition a detailed table of the more important contribution to the measurement of porosity since 1921 forms a conclusion.

Introduction.

The scientific study of porosity is of interest to many industrial and scientific bodies. The building trade is a major example of the first type: considerable sums of money and time have been spent, and much research into the porosity of media, such as cement, bricks and building stones, has been accomplished. A study of ceramics involves patient research into this property of pottery. Insulating porcelain prepared for electrical work should have a minimum of pore space, and, thus, an accurate method of measuring and studying the various variables that contribute to the porous state of matter is all-essential. Bacteriological and other investigations into the size of submicroscopical objects utilize the size of the pores in carefully prepared containers to give an approximation of the volumes such bodies occupy, by filtration, similar to the manner of grading sands by sieves. A further important practical use of porosity is found in adsorption processes, where the activity of the adsorbent is governed, to a large extent, by the amount and size of pore space the material possesses.

This paper is devoted to porosity problems intimately connected with the oil industry. Theories accounting for the origin, migration and the more appropriate geological structures for storing oil are in conflict with each other; but the fact remains that where and when oil is found it exists in the interstices of the reservoir rock. Since petroleum is a separate phase from the other minerals of the rock, and not in combination with them, the extent to which oil can be stored in a reservoir is a function of the porosity of that reservoir. It must be mentioned that the potential reservoir, or the amount of oil which can be recovered from the oil-pool concerned, has additional factors which may totally annul the effects of a

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high porosity. Thus a shale bed possessing a high porosity—40 per cent.—would, in most cases, compare very unfavourably in the production of oil with a sand, loosely cemented, of only 15 per cent. porosity. Two statements can be made concerning porosity and probable extent of oil in a reservoir. Firstly, a formation having zero porosity, and no joints or fissures, cannot store oil. Secondly, if all other variables were duplicated, the more porous of two formations would possess more oil. A third generalization, limited, however, by certain other considerations, is, the more porous of two otherwise similar reservoirs would be more productive.

It is clear that the study of the factors which tend to increase or decrease porosity and the actual measurement of this physical characteristic is of vital importance, since it affects the actual source of oil. To limit the scope of this research, a preliminary survey of the type of rocks which characterize the oil zones of big producing fields would assist in concentrating on particular rocks.

Origin of Porosity in Rocks.

A survey of producing fields, active or exhausted, shows that oil comes from sedimentary rocks, particularly from sands, sandstones, conglomerates, porous limestones and dolomites. Wherever oil occurs in quantity, impervious strata cover the deposits. The reservoir beds are almost invariably marine strata or strata of fresh-water origin which are closely associated with marine formations. It is put forward that the organic material from which petroleum originates is deposited in clays and marls, the oil accumulating in sands and other porous rocks that are generally associated with the clays and marls. Whether this outline of the origin and migration of oil is correct in every detail or not, the fact remains that the most common strata in the producing zones of oilfields are those in which shales, clays or marls alternate with thinner beds of sands.

The pores in reservoir rocks may be due to " primary " or " secondary " openings depending on whether these openings originated at the time the rock was formed, or later in the life of the rock as a result of subsequent phenomena. The primary openings in rocks may be classified into four groups: intergranular spaces, bedding planes, vesicular spaces and submicroscopic pores. The secondary openings may be due to one or more of four natural forces, all of which are destructive to the matrix of rocks. Openings may be formed by solutions, by shrinkage-cracks due to dehydration, cooling, etc., by thrust forces of crystallization from solution, or by greater earth movements which may exceed the crushing strength of the rock minerals and shatter them.

The intergranular spaces are the most important of the primary openings in so far as petroleum production is concerned. Nearly all the pore spaces in oil sands and sandstones are the interstices between the grains of the rock. Sands range in porosity from less than 1 per cent. to 25 per cent., and in some cases to even higher percentages. Buckley reports the porosity of the Dunnville sandstone as constituting 28·28 per cent. of the total volume.[1] Naestock sand has a maximum porosity of 34·2 per cent.,[2] whilst a 1937 Report [36] on Porosity of Sands shows a maximum porosity of 36·2 per cent. The primary intergranular spaces may increase or decrease through secondary porosity factors.

Bedding planes exist by virtue of the assortment or sizing of grains that build up the strata, such assortment being accomplished during transportation and deposition. On account of this sizing of material, there exists a different arrangement of pore spaces in the different beds.[3] The effect of this differentiation is more pronounced on permeability than on the porosity of the rock—that is to say, fluids would flow at a different rate across the bedding plane than they would parallel to it.

Vesicular spaces are found in igneous rocks, and are of little value to the oil industry. Magmas contain, besides minerals, certain fluids. After a volcanic eruption or shallow depth intrusion of magma, the pressure is relieved and the fluids escape as gases; should the gases expand when the lavas are in a viscous condition just above their solidification points, the passage of the gas is preserved. It is of importance to note a difference between this type of opening and the other two discussed. Vesicules in solidified lavas are either entirely closed or may have an outlet to the surface of the rock, but are not interconnected. Pores in a sandstone, on the other hand, are mostly interconnected and have access to the outside, only a portion of the spaces having no outlet. Thus, there are two types of porosity: "available" and "non-available" for the storage and passage of liquids. The sum of available and non-available porosities, both measured in percentages of total volume, constitute "total" porosity. There has been, unfortunately, a lack of differentiation between these three terms when values of porosities have been reported.

The fourth type of primary openings—submicroscopic spaces—are similar to the intergranular spaces, except in size. Such submicroscopic pores may exist in the grains that constitute the rock matrix, but are so small that surface-tension forces, and even molecular forces in the case of minute pores are too great to allow the easy passage of fluids. All matter has submicroscopic pores, but a notable case in the oil industry is the oolitic limestones, which have a porosity lying midway between that possessed by the intergranular and submicroscopic spaces. The pores are found in the grains or ooliths, and are in the form of minute channels similar to those of the Girvanella type of calcareous algæ.[4] They are large enough to be discerned under the microscope, after suitable staining, but are too small to allow easy passage of fluids through them. Thus, like the submicroscopic spaces, these pores are amongst the "non-available" porosity, although they may have access to the outside, so far as oil production is concerned. In porosity measurements, however, such will be returned as available or non-available, depending on their size and on whether gas or liquid is used in the porosimeter. This point again stresses the difference between porosity, which is a measure of volume irrespective of size, and permeability, which is a function not only of the volume of the voids, but also of their average size.

Porosities of sand formations are mainly due to primary openings formed when the sand was deposited. The other types of reservoirs, mostly limestone and dolomite and the few known examples of shales, igneous rocks, etc., hold oil in spaces formed subsequent to the deposition or solidification of the rock.

Solution of calcium and magnesium carbonate often results in large openings—underground rivers and caves are examples of this type of

porosity. Solution usually results in enlargement of already existing smaller openings, such as joints, bedding planes or fissures. The action of solution is more active above the water-table, but large cavities have been found well below the water-table which existed at some previous geological time. Where an ancient drainage channel is buried by strata of later date, solution cavities may be discovered at great depths. Oil may displace the water filling these cavities, and thus an oil-pool is formed in an otherwise compact limestone formation.

Weak acids may be other solvents for limestone. In the Trenton and the Asmari limestones the magnesium content of the formation decreases proportionately with depth. Weak acids dissolve calcium carbonate more rapidly than magnesium carbonate, and thus it is possible that humus acids have removed the lime from erosion surfaces to a greater extent than they have magnesium, making the limestone porous and increasing the proportion of magnesium in the upper layers.

Howard [5] has stated that probably 95 per cent. of the limestones owe their porosity to weathering. In Ohio, Indiana, Michigan, Ontario, Illinois, Kentucky and Tennessee, to mention only a few areas, practically every limestone reservoir lies within 100 feet of a superlying unconformity. Other fields, both in the United States and elsewhere, show the same proximity to an old erosion surface.

Churty limestones, upon weathering, lose most of the calcium carbonate by solution as bicarbonate, leaving a mantle of insoluble churt. In some of the oilfields of Kansas and Oklahoma the pores thus formed in the churt breccia have proved to be good reservoirs for oil. Many fields producing oil from eroded surfaces of limestone possess residual churt above the limestone which forms a considerable portion of the oil reservoir. In the more general cases the fissures and channels in the limestone itself form the reservoir.

Reservoirs in igneous rocks owe their origin to this mode of porosity, assisted by the second type of secondary pores—namely, openings due to shrinkage. Shrinkage may be due to cooling, dehydration and subsidiary chemical reactions between the minerals constituting the rock. The most outstanding of secondary reactions in oil reservoir formation is dolomitization.

The main reservoirs in Florence, Colorado, are in fractured shales that are not associated with sand. Similarly, in the Salt Creek field, Wyoming, considerable production of oil has been realized from fractured shales, although the chief reservoirs are in sands. Other fields depending in part on fractures in shale are found in California, while Lytton Springs oilfield, Texas and Totunio field, Venezuela, obtain oil from fissures in igneous rocks.

Porous limestone has been cited to illustrate porosity by solution, but another important factor is dolomitization. Orton, who studied the Trenton limestone of the Lima-Indiana oilfield and found it dolomitic where it contains oil, mentioned that its porosity was entirely due to the phenomenon of dolomitization. "Dolomite" designates the mineral species the composition of which is [$CaCO_3$,$MgCO_3$]. Dolomitic limestone, therefore, contains this mineral, but a "magnesium limestone" can exist containing both carbonates of calcium and magnesium in two independent

mineralogical forms not having the specific dolomitic form. Chemical interaction might then take place between these two minerals to form dolomite, but the volume of the dolomite is 12·5 per cent. smaller than the combined volumes of the parent minerals. This phenomenon of dolomitization will result in cavities in the limestone, and Orton has attributed the porosity of the Lima-Indiana field to such a phenomenon.

It is now known that replacement takes place by solution and deposition in fissures and openings so small that there is no collapse of the original structure.[4, 6] Phinney, who studied the same field as Orton, stated that the limestone porosity was due to loss of substance, and not to substitution. Bownocker confirmed the views of Orton, and so many other oilfields have been found in which the limestone was dolomitic that Orton's theory had

FIG. 1.

ENLARGED SECTIONS OF TRENTON LIMESTONE, SHOWING NATURE OF PORES.

some justification. Mylins and Jillson, working in Illinois and Kentucky, respectively, have noted, on the other hand, that numerous limestone reservoir rocks are found at old erosion surfaces.[2] The fact that the Trenton limestone decreased in magnesium content with depth has already received a tentative explanation on the basis of preferential solution of limestone at or near erosion surfaces.

It is quite possible that porosity in dolomitic limestone is due to both solution and dolomitization processes. This follows logically from two statements made previously. Firstly, dolomitization results in shrinkage, and secondly, dolomitization starts in solutions at fissures. It is clear, except in the few cases where evidence shows the direct precipitation of dolomite from solutions in the strata,[7] that these two processes have co-operated in forming cavities wherever dolomite exists in limestone. Again, it follows that pores formed either by solution or by dolomitization have their origin in shrinkage cracks. In fact, minute cracks in the rock,

developed consequent to the drying process of the sedimentary strata, are the origin of three of the four secondary openings.

The other two types of secondary openings due to crushing thrusts of crystals and tectonic disturbances are not as important to oil reservoirs as the first two types. Becker and Day [8] assumed that the force exerted on the containing walls by crystallization is sufficient to enlarge the space which encloses the solution. Thus rocks can become more porous by this process only if they possess open spaces to which a solution can gain admittance. Experiments by the same workers showed that the crushing strength of crystals is equal in magnitude to the thrust a crystal would exert on a surrounding wall preventing its crystallization. Harris [9] used the force of crystallization to account for the salt domes of the Gulf Coast, but later work proved that these domes were thrust upwards by tectonic forces.

Pores formed by the greater stresses inherent in the deformation of the crust of the earth are much more in evidence in metaliferous deposits than in oil reservoirs. Dikes of ozokerite, gilsonite and other bituminous materials have been formed by the drying-out of petroleum in such fissures, and the great gilsonite dikes of the Unita basin, Utah, rank amongst the greatest of their kind. Such fractures have proved effective channels for the migration of petroleum, from the beds in which it originated, to the reservoir rock.

In conclusion, primary intergranular spaces and secondary pores by solution represent the most important types of porosities when considering oilfield reservoirs.

Capacity of Oil Reservoirs.

The foregoing discussion on the types and origin of pores in oil-reservoir rocks reveals the fact that it is relatively more difficult to estimate the capacity of a limestone bed for holding fluids than it is for a sand or a sandstone. Cavities in limestone may be commensurable with the size of the sample under test, whilst the sample may reveal a hard, compact nature. Sands show the same irregularity, but to a lesser extent. Although "shoestring" sands and irregularly cemented sandstones are examples of irregularity in pore space of sands, Emmons has reported that, in general, this type of rock possesses a uniform porosity.

Slichter's [10] work on porosity has shown that a system of uniform spheres packed in the most compact manner will have a porosity of 25·95 per cent., independent of the size of the spheres. The same principle applies to sandstones of uniform grain size; the size of the grain does not appear to affect the porosity. Clays, the average grain size of which may be of colloidal dimensions, may possess very high porosity, as evidenced by the large quantity of absorbed water. Gradings of different sizes have the utmost significance, since smaller grains may fill the pores between the larger. Basic rocks, on weathering, yield clays to a greater degree than do acidic rocks. Thus sands derived from basic rocks will have smaller capacities for oil than similar sands resulting from, say, granite. The clay in the former type will fill more of the space between the sand grains, but many exceptions have been noted in producing-fields.[2]

In addition to the uniformity of grain size, the shape of the grains and

the mode of packing are equally important factors affecting the porosity. The manner in which these two factors affect porosity is most complex, and irregularly shaped grains may form a sand which possesses a porosity greater than, equal to or less than a system of uniform spheres. If the material is highly angular, with no flat laths, it is probably more porous than the regular system. Porosity is a property of matter that should be measured directly by special apparatus and correct technique, and not estimated from sieve tests, for the variables are complex in their relation to each other and to porosity.

In estimating the capacity of a reservoir, the over-all volume and porosity should be corrected by a saturation factor. Washburne [11] determined the saturation factors for two samples as 60 and 75 per cent., the remainder of the voids being filled with gas and water. It is impossible to extract all the oil, therefore, in estimating the total yield or the potential reservoir, other factors are involved. The two terms "capacity" and "yield" must be strictly differentiated. "Capacity" is a function of porosity, whilst "yield" is a function of porosity and permeability, excluding many other variables, such as viscosity, surface tension of the oil, etc.

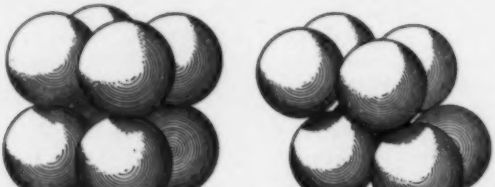
Quantitative Study of Porosity.

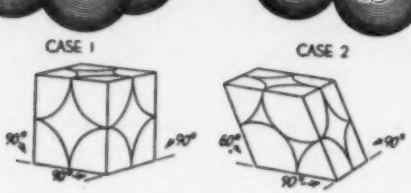
The quantitative study of porosity was first attempted on an ideal system by Slichter, who examined a porous medium composed entirely of spheres packed in various ways.[12] Smith, Foote and Busang [13] are more recent contributors, but the work of Graton and Fraser [14] appears to be the most comprehensive yet attempted on the subject. These two workers assumed for their analysis that the uniform spheres constituted the matrix of an unconsolidated sand body. Six cases or modes of packing may be classified, each forming a geometrical solid for a unit cell, but the two most interesting forms are those which have the greatest and least porosities, respectively. Unit cells of *cubic* packings possess the greatest porosity, whilst *rhombohedral* packings possess the least. By filling the pores with plaster of Paris, a mould may be made, and a number of these units placed consecutively gives a true picture of the pores. The volume of the pores can be calculated from the geometry of the figure, or actually measured by immersing the mould in a liquid. The maximum porosity—that of a *cubic* packing—is 47·64 per cent., whilst the minimum value—viz., a *rhombohedral* packing—is 25·95 per cent. Porosity here means the ratio of the volume of the voids of a unit cell to the total volume of the cell.

Theoretically the size of the sphere does not affect the porosity value for any form of packing. After a reasonable amount of agitation, it may be expected that the particles of sand would possess the most stable form of packing—namely, *rhombohedral*. Actual tests, however, do not substantiate these two statements. Ellis and Lee [15] found the following general measurements of porosities :

Coarse sand	39–41 per cent. porosity.
Medium sand	41–48 ,, ,,
Fine sand	44–49 ,, ,,
Fine sandy loam . . .	50–54 ,, ,,

Smaller particles varying in size from 0·02 mm. to 0·002 mm. may possess porosities from 50 to 95 per cent.[16] These figures also demonstrate the scarcity of *rhombohedral* packings in natural sands.





Unit cells of cubic (case 1) and rhombohedral (case 2) packing.

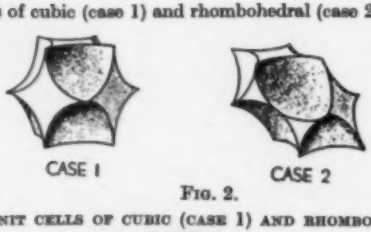


FIG. 2.

PORES OF THE UNIT CELLS OF CUBIC (CASE 1) AND RHOMBOHEDRAL (CASE 2) PACKING.

(After Graton and Fraser, *J. Geol.*)

The porosity of a solid body has been observed to be governed by factors that are too variable in character and too elusive in definition to permit an accurate calculation to be made of the available or total porosities. The only possible way in which the values of the porosities of rocks can be determined with any degree of accuracy is by measuring them directly.

MELCHER'S METHOD (cf. Uren [17]).

One of the earlier methods of measuring porosities, and credited by Muskat [18] to be the most accurate, is Melcher's gravimetric method, which is capable of giving an accuracy of $\pm$ 1 per cent. porosity on a fragment that weighs 0·1 oz.[19] The method is based on the relationship:

$$P = 100\left(1 - \frac{V_g}{V_b}\right)$$

where P = total porosity in percentage, V_g = volume of grains that constitute the matrix, and V_b = bulk volume of the sample.

Loose particles are brushed from the rock after the oil has been extracted

and the sample dried. The temperature of drying is of importance, and should not be high. Honess and Heyl [20] have shown that the porosity increased by 4 per cent. on the value taken at 110° C. when the sample was heated to 200° C. The increase of porosity with temperature is greater with higher temperatures, the maximum recorded increase in porosity being 143 per cent. at 800° C., of the value obtained when the sample was heated to 110° C.

After cleaning and drying, the sample is broken into two pieces, one for the determination of the volume of the grains, and the other for bulk. One portion is weighed and dipped in molten paraffin wax to give a uniform coating. The temperature of the wax should be only a few degrees above its melting point, and time of dipping must not exceed two seconds, to prevent penetration of pores. Paraffin wax entering the pores can be detected by small gas bubbles in the wax. The surface is examined for small holes, and any present can be closed by a hot wire applied gently to the wax. The coated sample is weighed, and the difference between this weighing and the first is the weight of wax. From a knowledge of the density of the wax the volume of the layer may be determined.

The coated fragment is suspended from a thin wire and weighed in distilled water. The temperature of the water is read during this operation. The sample is dried, weighed in air, and any increase in weight is due to water having been absorbed by the sample through the cracks in the wax covering. After corrections have been made for absorbed water and the weight of the wire, the volume of the coated sample is calculated in the ordinary way—*i.e.* the difference in weight of coated sample in air and water divided by the density of the water at the recorded temperature. The bulk volume of the fragment is the difference between total volume of the coated sample and the volume of the wax layer. The sample is broken and examined to see whether wax has penetrated the material, and, should penetration have taken place, the experiment must be repeated.

The second part of the sample is weighed and crushed into its component grains, using a microscope to check the size of the particles until they are of the order of the grain volume.

The material is transferred and weighed in a pyknometer, preferably of the Johnston and Adams type,[21] the weight of which, empty and filled with water, is known. Two-thirds of the remaining volume of the pyknometer unoccupied by grains is filled with distilled water. Air is eliminated from the sample grains either by applying vacuum or by boiling the water in the pyknometer, but the latter method has many objections. When all the air is driven out, the remaining space is filled with water, and the pyknometer is weighed at a definite temperature. Thus the weight of the water displaced by the sand grains will be known, and the volume of the grains can be determined.

Finally, from the weight and volume of the first portion the volume of a unit weight of rock is computed. Similarly, from the volume and weight of the grains the volume of the grains of the same unit weight of rock is calculated. The difference in the two volumes gives the volume of pore space, and this divided by the bulk volume of a unit weight of rock and multiplied by 100 gives the total porosity in percentage.

It will be noticed that the sample, or a major part of it, is reduced to

loose grains, and no further tests can be made on this sample for the effect of certain factors on porosity. As an illustration, the effects of acid treatment of rocks using various concentrations, time factors, temperature, etc., cannot be studied on the same sample if this method is adopted. Porosity in the same sand varies widely within short distances, and this fact makes the procedure of measuring porosity of two different samples of the same specimen—one before and the other after treatment—quantitatively untrustworthy. Another method, therefore, which does not involve the crushing of samples must be employed.

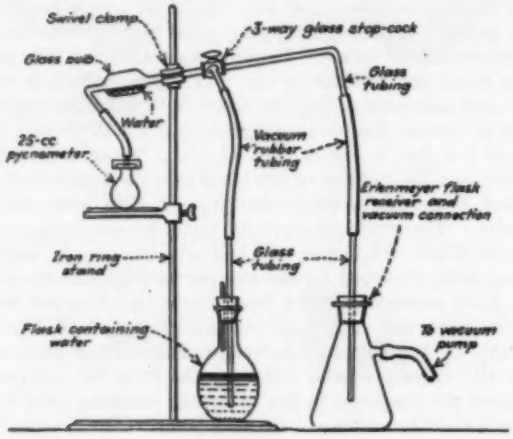


FIG. 3.

AVAILABLE POROSITY.

Available porosity can be measured without crushing. Fluids absorbed in the voids are subjected to volume measurement, and this volume divided by the bulk volume of the sample gives the fractional porosity of the material. Liquids or gases can be utilized for assessing the volume of the voids.

Reilley and Rae [22] describe many volumenometers for finding the volume of irregularly shaped solids using air as filling medium. All forms rely on Boyle's Law, the pressure of an enclosed and known volume of air being read before and after expansion into a chamber of known volume containing the sample. Its volume is calculated by assuming that isothermal expansion has taken place. An interesting volumenometer is Surdo's apparatus, which is capable of attaining an accuracy of 0·1 per cent.; but no published work shows its application to porosity measurement.

Washburn and Bunting. Washburn and Bunting published a series of papers in 1922 dealing with porosity measurements, in which they adopted methods utilizing air under isothermal conditions of expansion to measure the available, or what the authors termed "virtual" porosity.[23] In the "general method" (see Fig. 4) two vessels of known volumes are connected

through a tap, and a manometer is connected to the vessel which holds the test-piece, and the tap is closed; thus air under atmospheric pressure is trapped in Chamber A. Vessel B, containing the sample, is evacuated to 20 mm., and the pressure is read on the manometer. The two vessels are then connected through the tap; thus air under atmospheric pressure in A expands and the pressure of the total volume of A and B is read again on the manometer. These pressure readings, the barometer pressure and the determination of the volumes of A and B are sufficient data to calculate the apparent volume of the enclosed rock. Thus let

V_1 = volume of B in c.cs.
V_2 = volume of A in c.cs.
V = apparent volume of sample—*i.e.* excluding voids in c.cs.
P_1 and P_2 the first and second values of absolute pressures in mm. Hg and B_P = barometric pressure in mm. Hg.

Then $P_1(V_1 - V) + B_P V_2 = P_2(V_1 + V_2 - V)$.

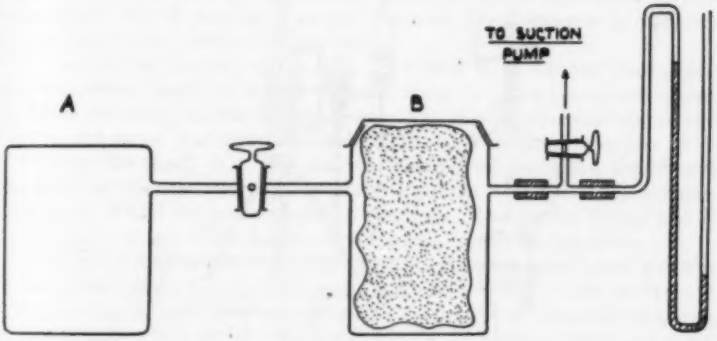


FIG. 4.

As all values except V are known, the apparent volume of the sample is readily calculated.

The bulk volume is found by Melcher's dipping method, and the available porosity is calculated according to the formula:

$$P = 100\left(1 - \frac{V}{V_B}\right)$$

where P = available porosity in percentage, and V_B = bulk volume of sample in c.cs.

The authors also describe a "rapid method" for measuring available porosity. In this apparatus the volume of the air in the voids is directly measured in a graduated tube under 1 atm., thus the procedure is similar to measuring pressures by McLeod's Gauge in a modified form.[24] The chamber A in Fig. 5 is the sample container; B is the expansion chamber to which a graduated capillary is joined.

The sample is put into A, B is fitted in position and the tap on B opened. Mercury is raised until it reaches a point above the tap, when the latter is

closed. Air is trapped in the sample, and thus when the mercury is lowered below the sample, the air expands into *B*. The reservoir is raised again, trapping air at lower pressure in the sample and compressing the air in *B* into the capillary. By adjusting the level of the mercury inside to that outside the apparatus, the pressure inside is 1 atm., and the volume of air under this pressure is read directly. This air is then expelled and the procedure repeated on the remaining trapped air, until the volume of air left in the sample is negligible. The sum of the air volumes is the volume of the voids. The bulk volume is determined for the sample, and from this the available porosity is obtained by means of the formula :

$$\text{Available porosity} = \frac{\text{volume of voids}}{\text{Bulk volume}} \times 100$$

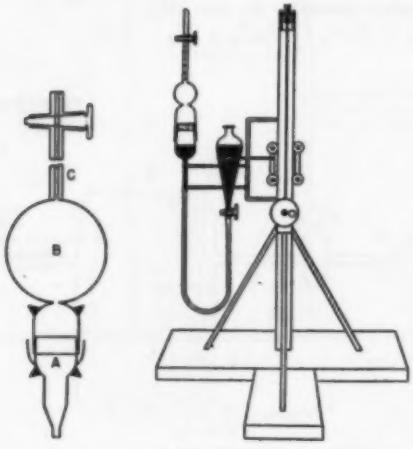


FIG. 5.

This method was advocated as suitable for measuring the porosities of highly cemented and compact bodies.

A criticism of this apparatus is that the mercury is allowed to come in contact with the sample. With sandstones this practice fouls the mercury, which tends to adhere to glass and sample, thus possibly closing a part of the voids, resulting in a reduction of the value of the available porosity.

In 1926 different authors proposed various methods for measuring the bulk volume. MacGee [25] utilized an air-expansion porosimeter similar to the one described, and he measured the bulk volume by enclosing the sample in the chamber and filling the remainder of the space with mercury from a burette. Westman [26] proposed measuring the buoyancy of mercury when the sample is immersed to a definite depth. Thus the amount of mercury entering the surface pores is standard. This operation is valuable for large volumes. Similarly, the method used by Hartmann, Westmont and Morgan [27] for measuring bulk volume by using fine zircon sand (124–148 mesh) is of interest only to those interested in bulk volumes

of bricks or other large bodies. The error on a volume of 1650 c.cs. after 200 repetitions was not more than 0·06 per cent.

Russell's Method. Russell evolved a volumenometer utilizing tetrachlorethane as the filling medium to determine the bulk volume directly.[28, 29] Tetrachlorethane is preferable to water because it enters pores more readily than the latter, drains out more quickly, and, further, sandstones which would disintegrate in water remain intact for months when immersed in it. Carbon tetrachloride, benzene and diethylether possess the same advantages over water, but their high volatility renders them less useful than tetrachlorethane for this purpose.

The special pyknometer illustrated in Fig. 6 has the two parallel tubes graduated in c.cs. whilst the two reservoirs have nearly equal volumes when the stopper S is fitted into place. Reservoir B and stopper S are connected by a ground joint. The tubes are held vertically with B uppermost, S is taken off and reservoir A is filled up to mark N, the zero point. Stopper S is then placed on to B, and the apparatus is inverted. The tetrachlorethane drains into B, and should reach M, if the apparatus is well constructed; but if this mark is not reached, the difference in the two volumes is recorded as the zero correction.

The sample is cleaned, dried and immersed in a beaker containing tetrachlorethane until air ceases to issue from it. The procedure is not affected if air is left in the sample, so long as this air remains inside and occupies the same volume. Meanwhile, the pyknometer reservoir A is filled up to the mark N. The sample is removed from the liquid and transferred to the reservoir B after excess liquid is removed. The stopper is put on to B and the pyknometer is inverted. The liquid drains into B and the bulk volume of the sample is recorded directly on the tube.

The sample is taken out, dried, crushed into its component parts and the volume of the grains taken in the same way with modifications to exclude air from being trapped between the grains. The loss of material on grinding can be taken into account by weighing the fragments before and after grinding and working on unit weight of rock. Then:

$$\text{Total porosity (per cent.)} = \left(1 - \frac{V_g}{V_B}\right) 100$$

where V_g = volume of grains in sample of unit weight, and V_B = bulk volume of unit weight of sample.

The method requires skill in manipulation, and is not so accurate as Melcher's Method. According to this investigator, it is quick and gives a good average if many samples of the same rock are tested. Russell found that the porosity of a sandstone by this method was 16·4 per cent., the average of six determinations varying from 15·5 to 17·2 per cent. Melcher determined the porosity of the same rock, and obtained 16·3, 16·1, 16·2 and 16·5 per cent.; the average was therefore 16·4 very approximately.

Barnes' Modification. A modification of Russell's method yields the available porosity. Barnes[19, 34] extracted the oil with carbon tetrachloride, and the weight of the sample free from solvent was determined accurately. The sample was then submerged in a beaker half full of tetrachlorethane, and the beaker subjected to vacuum. After bubbles had ceased to issue from the sample, air was admitted, and an accurate

weighing of the saturated sample yielded the increase in the weight of the fragment due to the weight of absorbed liquid. The increase in weight divided by the density of the liquid at the recorded temperature is the volume of the voids. The bulk volume was found by Russell's method and

$$\text{Available porosity (per cent.)} = \frac{\text{wt. of sat. sample-wt. of dry sample}}{\text{Density of liquid} \times \text{bulk volume}} \times 100$$

Errors due to temperature effects are the more important, and Russell advocated the use of gloves for handling his pyknometer.

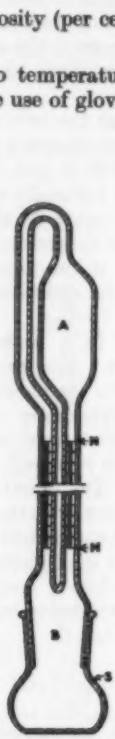


FIG. 6.

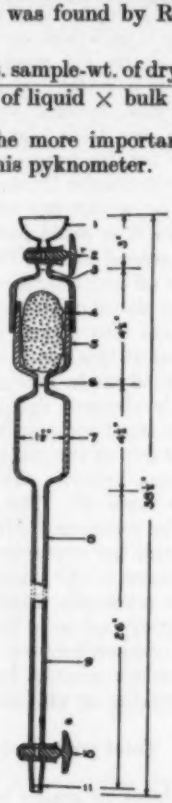


FIG. 7.

Nutting [30] (1930) reverted to Melcher's method, modified by finding the densities instead of total and grain volumes. Nutting claims that even a prolonged extraction of oil by hot solvent is not effective in removing all the carbonaceous matter, and advocates ignition in an ordinary bunsen burner, *circa*, 800° C. The results of Honess and Heyl's [30] investigations into the effect of high temperatures on porosity, already mentioned, throw grave doubts on such a procedure. After cleaning, the sample is coated with wax and the bulk density found by means of a pyknometer using " tetralin " (tetrahydronaphthalene). Nutting found that quartz adsorbs water and may cause as much as 1–2 per cent. error in the apparent grain density. The absorbed film of water is about 10^{-5} mm. thick, and has density of 1·3 gms./c.c. Tetralin is not adsorbed, and since it is a solvent

for both oil and water, it wets the grains, and there is less likelihood of air bubbles attaching themselves to the grains. When the bulk density γ_B and grain density, γ_g are found,

$$\text{Total porosity} = 100\left(1 - \frac{\gamma_B}{\gamma_g}\right)$$

Tickell, Mechem and McCurdy [31] have correlated the porosity of unconsolidated sand bodies to size ratio of binary and ternary mixtures, to angularity of grains and to variation of compaction. A more important feature of their contribution, however, is the development of a gas-expansion glass porosimeter (see Fig. 7).

The principle of the apparatus is that the apparent volume of the sample can be measured by placing the sample in the upper chamber when mercury is at mark 6, closing tap 2, thus trapping a volume of air at 1 atm.; if the mercury is allowed to run out from tap 10 into a dish, keeping the level of mercury in the dish at mark 11, then the height of the mercury column between 11 and its level in the graduated tube 8, 9 is a function of the volume (for any one barometric pressure). Should known volumes have been placed in chamber 5 and corresponding readings on the graduated tube taken, then a calibration curve can be plotted connecting graduations with volumes, and thus the apparent volume of the rock is read directly from the curve. The expansion is according to Boyle's Law, and hence temperature variation during the test introduces serious errors. Bulk volume is measured either by coating the specimen with celluloid dissolved in amyl acetate and repeating the procedure, or filling the upper chamber with mercury and finding the amount of mercury displaced by the sample.

$$\text{Available porosity (per cent.)} = 100\left(1 - \frac{\text{Apparent Volume}}{\text{Bulk Volume}}\right)$$

The same principles which govern Washburn and Bunting apparatus are the bases for this modified form, and the same mathematical calculations (with regard to apparent volume from pressure readings of the air before and after expansion) apply.

Hydrogen Porosimeter.

Coberly and Stevens [32] have utilized another gas-expansion porosimeter based on the isothermal expansion of an inert gas. These investigators chose hydrogen, since (1) it obeys the gas laws more closely than other gases, (2) " it readily penetrates the sample " and (3) it is less adsorbed by solids and liquids. The apparatus (see Fig. 8) is made of steel, and high pressure is employed. The gas is allowed to expand to fill a larger space, and from the two gauge pressures and the known volumes of the intercommunicating chambers (one of which contains the sample) the apparent volume of the rock is calculated on similar lines to those explained previously. This method is rapid, and it is claimed that an error of 1 per cent. on a 20 per cent. porous sand results from an error of 0·5 lb. in reading the pressure gauge. These investigators advocate the same principle formulated by Russell—viz., a rapid and less accurate method of porosity measurement is to be preferred to a slow and more accurate one. The bulk volume

of the sample is measured by displacement of mercury in a wide-mouthed pyknometer.

Recent Methods.

It is of interest to note that Thomas and his collaborators [33] (1935) developed a similar high-pressure porosimeter. Air under high pressure (up to 45 lb./sq. in.) was enclosed in an upper chamber and the pressure read on a constant-volume mercury manometer. The compressed air was then allowed to expand into a larger chamber containing the core, and the pressure noted. The volume of the two chambers being known, the apparent volume was calculated as indicated before. The bulk volume

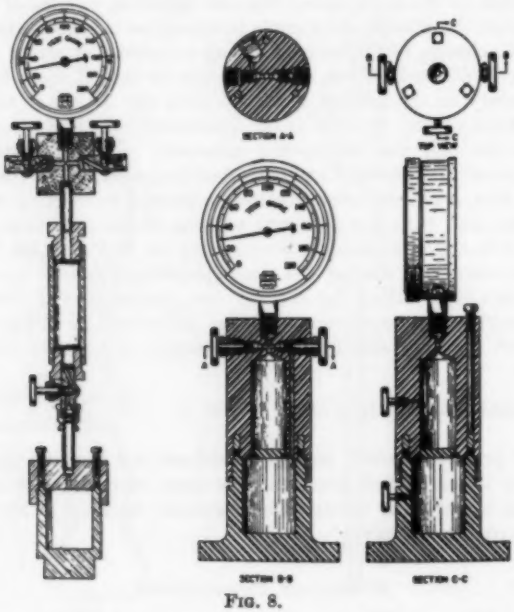


Fig. 8.

was determined by actual mensuration of the turned limestone core. These investigators also developed a pyknometer method, in which "recrystallized" benzene was absorbed in a similar manner to Barnes' method.[34] These workers state that the absorption method gives more repeatable results than the high-pressure gas-expansion method.

Froome [35] also describes a high-pressure method (75–100 lb./sq. in.), and arrives at the conclusion, after reviewing many other processes, that a quick and *fairly* accurate method is to be preferred to other types, since the porosity of a sand changes so rapidly with location. The Petroleum Experiment Station of the Bureau of Mines, Bartlesville, Oklahoma, have adopted an apparatus in which air under 40–200 lb./sq. in. is expanded to atmospheric pressure, and the final volume rather than the pressure of the air is measured in order to determine the apparent volume of the core.[36]

Comparison of Various Methods for Porosity Measurements

Worker.	Date.	Type of Porosity.	Chief Items in Apparatus.	Fluid Used.	Bulk Vol. Measurement.	Formula for Porosity.	Remarks.

Comparison of Various Methods for Porosity Measurements

Worker.	Date.	Type of Porosity.	Chief Items in Apparatus.	Fluid Used.	Bulk Vol. Measurement.	Formula for Porosity.	Remarks.
Melcher.	1921	Total.	Analytical balance.	Distilled water.	Covering with wax and weighing.	$P_T = 100\left(1 - \frac{V_g}{V_B}\right)$.	Accurate; slow; sand reduced to grains.
Washburn–Bunting.	1922	Available.	Glass chambers, manometer and barometer.	Air.	Melcher's method.	(1) $P_A = 100\left(1 - \frac{v}{V_B}\right)$. (2) $P_A = 100\frac{v'}{V_B}$.	Mercury fouled resulting in increasing errors.
MacGee.	1926	Available.	Washburn–Bunting.	Air.	Displacing mercury.	$P_A = 100\left(1 - \frac{v}{V_B}\right)$.	Same as Washburn–Bunting.
Hartmann, Westmont and Morgan.	1926	Available.	Washburn–Bunting.	Air.	Displacing fine zircon sand.	$P_A = 100\left(1 - \frac{v}{V_B}\right)$.	Only for large volumes.
Russell.	1926	Total.	Special pyknometer.	Tetrachlorethane.	Displacing tetrachlorethane.	$P_T = 100\left(1 - \frac{V_g}{V_B}\right)$.	Rapid but not highly accurate; sample reduced to grains.
Nutting.	1930	Total.	Analytical balance.	Tetralin.	Melcher's method.	$P_T = 100\left(1 - \frac{\gamma_B}{\gamma_g}\right)$.	Accurate; slow; sample reduced to grains.
Barnes.	1931	Available.	Russell's pyknometer. Analytical balance.	Tetrachlorethane.	Russell's method.	$P_A = \frac{W_S - W_D}{\gamma \text{ liq.} \times V_B} \times 100$.	Uncertainty in handling samples.
Tickell, Mochem McCurdy.	1933	Available.	Glass chambers and barometer.	Air.	Covering with celluloid or mercury displacement.	$P_A = 100\left(1 - \frac{v}{V_B}\right)$.	See Part II of this series of Papers.
Coberly–Stevens.	1933	Available.	Steel bomb and gauge.	Hydrogen under pressure.	Displacing mercury.	$P_A = 100\left(1 - \frac{v}{V_B}\right)$.	Quick but not highly accurate. Portable.
Thomas, Chisholm and Cameron.	1935	Available.	(1) Steel bomb and gauges. (2) Special pyknometer.	Air under 45 lb. per sq. in. "Recrystallised" benzene.	(1) Mensuration. (2) Mensuration.	(1), (2) $P_A = 100\left(1 - \frac{v}{V_B}\right)$.	(1) is quicker than (2); but (2) gives more repeatable results.
Froome.	1936	Available.	Steel bomb and gauges.	Air under 75–100 lb. per sq. in.	Any of above.	$P_A = 100\left(1 - \frac{v}{V_B}\right)$.	Quick but not highly accurate; portable.
Buwalda.	1936	Available.	Glass chambers.	Air.	Mercury displacement.	$P_A = 100\frac{v'}{V_B}$.	Portable.
Taliaferro, Johnson and Dewees.	1937	Available.	Steel bomb, gauges. Special pyknometer.	Air under pressure up to 200 lb. per sq. in.	Mercury displacement.	$P = 100\left(1 - \frac{v}{V_B}\right)$.	Accurate to ±0·25% on porosity measurement.

An interesting portable apparatus, developed by Buwalda,[37] determines the bulk volume by measuring the volume of mercury displaced by the sample, the volume of the voids by repeatedly expelling the air from the void and measuring the volume under atmospheric pressures. It is, thus, similar in principle, though not in detail, to the original gas expansion method of Washburn and Bunting as modified by Fancher, Lewis and Barnes.[23, 38]

Muskat [18] gives tables comparing results of porosity measurements obtained, by four fundamental methods—Melcher's, Russell's, Washburn-Bunting's and Barnes'. The discrepancies and agreements are of interest.

Sand.	Locality.	Total Porosity.		Available Porosity.	
		Melcher–Nutting.	Russell.	Washburn–Bunting.	Barnes.
Stockton.	Stockton, N.J.	—	1·3	—	1·2
Stockton.	Lumberville.	—	4·3	—	4·3
3rd Venango.	Oil City.	11·1	9·8	—	—
3rd Venango.	Oil City.	14·3	14·5	—	—
Clarendon.	Warren.	—	10·0	9·9	9·3
Clarendon.	Warren.	—	12·6	12·2	11·8
3rd Bradford.	Bradford.	—	16·9	15·3	15·0
3rd Bradford.	Bradford.	14·1	13·4	12·8	12·5
3rd Bradford.	Bradford.	13·6	13·5	13·3	12·8
3rd Bradford.	Bradford.	16·1	15·7	15·4	14·9

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Oil Engineering & Refining Department,
University of Birmingham.

THE APPLICATION OF PHYSICO-CHEMICAL PRINCIPLES TO THE INVESTIGATION OF THE PROPERTIES OF ROCKS.

PART II.

APPARATUS & TECHNIQUE FOR POROSITY MEASUREMENT.*

By A. H. Nissan, B.Sc. (Student), C. E. Wood, M.Sc., A.I.C. (Member), L. V. W. Clark, M.Sc., M.I.Mech.E. (Member) and A. W. Nash, M.Sc., M.I.Mech.E. (Member).

Synopsis.

The main object of this research is to attain accuracy in porosity determination and hence the paper is concerned with detailed technique. Two methods are put forward for determining bulk volume of rocks to an accuracy of 0·2%, namely a micrometer and a modified pyknometer method. After the determination of total porosity by a special pyknometer method it is concluded that certain losses, difficult to control, render total porosity a less satisfactory measure for the effects of physico-chemical treatments of rocks than available porosity. Still, measurements of total porosity are reproducible to $\pm 0{\cdot}25\%$.

Available volume is determined by a liquid absorption method and also by a gas-expansion porosimeter. The effects of several variables are analysed and the reasons for deviations in the design of the porosimeter from conventional practices are indicated. Finally the minimum bulk volume to give a maximum error on porosity measurement of $\pm 0{\cdot}25\%$ is calculated assuming the worst possible conditions. The apparatus generally gives double the accuracy expected. The authors consider that both methods for determining available porosity of rocks with respect to accuracy, simplicity and speed of working can be compared favourably with previous methods. It is to be regretted that few workers in this field have discussed quantitatively the accuracy of their respective methods.

The object of the research was to develop a method for the measurement of available and total porosities giving a higher accuracy than other known methods. The accuracy reported by the latest method (Report by the United States Bureau of Mines, R.I. 3352, September, 1937) was $\pm 0{\cdot}25$ per cent. Thus a reported porosity of 17·25 per cent. may have the value of 17·00 or 17·50 per cent. The apparatus and technique should have, therefore, at least this accuracy, in order to provide a check on the Bureau's method.

The total porosity determination has the inherent drawback of reducing the sample to grain size, and hence cannot be used as an accurate method of measuring the subsequent effects of chemical or physical treatments on a rock sample. An available porosity method should therefore be used, which would not affect the sample and which would be a useful measure of such treatments.

Three quantities have to be determined: bulk volume, actual volume of solid grains, and apparent volume (total volume minus volume of available pores) of the sample.

* Paper received May, 20th 1938.

Bulk Volume.

Preparation of the Sample.—The most important measurement methods for bulk volume are :—

(1) Coating the sample with wax, celluloid, etc., and measuring the enclosed volume.
(2) Using a pyknometer with mercury as the displaced liquid.
(3) Mensuration.

Whichever method is used, a concave cavity in the surface of the sample will tend to produce an error, due to the bridging of this cavity by the liquid or solid employed for measurement of volume. Owing to this possible error, it was decided to form truly, or as truly as possible, cylindrical samples for the tests.

A cutter was developed which did not collect the dust between the tool and sample and thus shear the test-piece prematurely. The cutter shown in Fig. 1, fixed to an ordinary drilling machine and running at low speeds formed the cylindrical samples as required. The feed may be manual or automatic, provided it is not excessively fast. Air under slight pressure was found to be advantageous with limestone, in that the dust was removed, and thus no seizure ensued.

An alternative method was to fit a motor-driven grinding-wheel on to the saddle of a lathe and to grind the sample to appropriate dimensions. The flat end in both cases was cut by hand.

In Part I the adverse effect of high temperatures on porosity measurement was mentioned (Honess and Heyl). The formation samples therefore were not subjected to a higher temperature than 80° C., and oil was extracted consequently by benzene in an ordinary extractor, after subjecting the sample to a vacuum (*circa* 10–20 mm. Hg) to remove loose particles of dust from the surface. Samples of 30 mm. diameter and 25 mm. height, after six hours extraction with benzene still discoloured an organic solvent (tetrachlorethane) when they were immersed in the solvent for 12 hours in the cold. The extraction period was doubled, and samples, originally rich in oil left both tetrachlorethane and benzene colourless after a 12-hours test immersion. Hence 12-hour extraction was adopted as the standard procedure for all samples of the above dimensions. When the length was doubled, extraction periods of 18–24 hours were found sufficient, and a 24-hours extraction period with benzene was adopted for samples measuring 30×50 mm.

Drying the test cylinders in hot air might result in the dehydration of certain hydrated component minerals of the rock, and might affect the porosity value by shrinkage. A drying apparatus was used which allowed air at 22–25° C. and 60–100 mm. pressure to pass continuously over the sample (Fig. 3). Suction was applied by a water-pump, and air was allowed to enter the apparatus through a small needle valve at the other end. The resistance to flow could be increased or decreased by means of this valve, and efficient and constant regulation of the vacuum was obtained. The air was passed through concentrated sulphuric acid, through a heating coil immersed in a paraffin oil-bath at 110–120° C. and finally through cotton wool. A $CaCl_2$ tube between the drying-tube and the water-trap

was used to prevent access of water vapour through back pressure. Benzene (vapour pressure 100 mm. 21·8° C.) is above its boiling point at the prevailing vacuum and temperature. A drying period of 4 hours was sufficient for the smaller samples, whilst a period of 8 hours sufficed for the larger samples. The odour of the solvent proved to be a good indication of the absence of the solvent in the sample. When approaching complete dryness the sample, when brought out of the drying-chamber into the atmosphere gave no odour, but after a short time a definite odour developed. Non-development after, say, 15 minutes, is a positive indication of complete absence of the solvent. This precaution should be taken, since the sample must have no vapour pressure when used in the gas-expansion porosimeter.

Measurement of Bulk Volume.—Three methods for determining bulk volumes were attempted : coating with wax (Melcher), micrometer and pyknometer method. Melcher's method was discarded for the following reasons :—

(1) The time taken for wax extraction and sample drying was excessive, and this procedure affected the bulk volume. Extraction was necessary in order to find both the apparent and grain volumes of the same sample, and not of another sample taken from the core.

(2) The uncertainty regarding wax penetrating the pores could only be removed by breaking the sample in many places and by an examination of the interface, a procedure which could not be followed for the same reason as in (1).

(3) De Khotinsky wax was tried as a substitute for paraffin wax, as it offered two advantages. The bulk volume could be measured in a gas-expansion apparatus which would also measure the apparent volume, whilst ordinary wax and celluloid could not withstand the differential pressure; and, further, the wax could readily be chipped off. This wax, however, introduces errors due to thickness of film, entrapping of air bubbles, opaque character and tendency to change its properties when heated either above 140° C. or continuously at lower temperatures. The wax showed a tendency to abstract sand grains from the surface when stripped off the sample.

Micrometer.—The type used was calibrated in millimetres and capable of reading to 0·001 mm. The height was measured in seven planes, and the diameter was measured five times in each of four different planes. The average height and diameter were used for calculating the bulk volume, assuming the sample to be a perfect cylinder. Table I gives typical readings of heights and diameters on the two sizes used.

To determine the reproducibility of bulk-volume measurement by this procedure, samples were measured successively with no treatments, and with saturation with benzene and tetrachlorethane and drying between each measurement. Tables II and III give typical results obtained.

It was concluded that :—

(1) Micrometer measurements for bulk volumes of rock gave reproducible results (and independent of operator) with a maximum deviation from the mean of $\pm$ 0·03 c.cs.

(2) No effect was noticeable on the sample when it was saturated with benzene and subsequently dried in the manner described. Thus

TABLE I.

Heights in Cms.

Sample.	Readings.							Average.
	1.	2.	3.	4.	5.	6.	7.	
I	2·5610	2·5615	2·5518	2·5492	2·5469	2·5476	2·5568	2·5535
II	5·0660	5·0815	5·0790	5·0659	5·0638	5·0678	5·0752	5·0713

Diameter in Cms.

Plane.	Readings.					Average for plane.	Average for sample.
	1.	2.	3.	4.	5.		
				Sample I			
1	2·9688	2·9672	2·9670	2·9661	2·9675	2·9673	2·9678
2	2·9675	2·9703	2·9635	2·9682	2·9670	2·9673	
3	2·9714	2·9680	2·9679	2·9661	2·9671	2·9681	
4	2·9706	2·9683	2·9682	2·9681	2·9672	2·9685	
				Sample II			
1	2·8550	2·8660	2·8802	2·8962	2·8617	2·8713	2·8695
2	2·8791	2·8780	2·8675	2·8642	2·8810	2·8739	
3	2·8782	2·8785	2·8565	2·8505	2·8785	2·8685	
4	2·8341	2·8711	2·8838	2·8828	2·8500	2·8643	

TABLE II.

Sample.	Average Diameter cms.	Average Height cms.	Volume, c.cs.	Remarks.
S1	2·9668	2·5415	17·569	Average volume = 17·54 c.cs.
S1	2·9650	2·5399	17·537	Maximum deviation = ± 0·03 c.cs.
S1	2·9661	2·5394	17·547	The sample was subjected to volume measurement by mercury between each mensuration.
S1	2·9638	2·5395	17·521	
S1	2·9644	2·5398	17·529	
S2	2·9772	2·5528	17·773	Average volume = 17·753 c.cs.
S2	2·9769	2·5506	17·754	Maximum deviation = ± 0·02 c.cs.
S2	2·9755	2·5502	17·734	No treatment between measurements.
S3	2·9680	2·5433	17·593	Average volume = 17·589 c.cs.
S3	2·9685	2·5425	17·595	Maximum deviation = ± 0·009 c.cs.
S3	2·9661	2·5423	17·580	No treatment between measurements.
S4	2·9719	2·5531	17·712	Average volume = 17·719 c.cs.
S4	2·9742	2·5556	17·750	Maximum deviation = ± 0·03 c.cs.
S4	2·9699	2·5545	17·697	No treatment between measurement.

TABLE III.

Sample.	Volumes.					Average Volume.	Maximum Deviation.
	1.	2.	3.	4.	5.		
Benzene Treatment between Measurements.							
I	17·741	17·701	17·706	17·704	17·694	17·709	± 0·02
II	17·722	17·770	17·731	17·706	17·716	17·729	± 0·04
III	17·687	17·656	17·670	17·666	17·664	17·669	± 0·02
Tetrachlorethane Treatment between Measurements.							
I	17·788	17·788	17·747			17·774	± 0·03
II	17·829	17·809	17·742			17·793	± 0·05
III	17·715	17·628	17·583			17·642	± 0·07

benzene is a suitable liquid for porosity measurements by liquid absorption methods, provided it satisfies other requirements.

(3) When tetrachlorethane is used, the volume shows a slight but definite reduction, which may be due to the higher temperatures and longer time which is necessary to free the sample from solvent. Tetrachlorethane is not suited to porosity measurements.

(4) Where the sample is chipped at the edges, the micrometer method is not suitable. Limestone samples, and certain sandstones, have a tendency to break at the sharp edges of the cylinder, and these small cavities will not be recorded by the micrometer; therefore another reliable method had to be employed.

Pyknometer Method.—The Bureau of Mines Report describes a mercury pyknometer which has enabled the operator to obtain 90 per cent. of 200-bulk-volume determinations accurate to 0·2 per cent. A similar but slightly modified pyknometer was designed and a similar procedure followed in this research. The results obtained confirmed the Bureau's claim as to accuracy.

The pyknometer (Fig. 4) consists of lower and upper portions, separated by a flat ground joint. The upper portion has a sloping top terminating in a capillary tube, whilst the lower portion ends in a two-way tap which connects the pyknometer to the atmosphere or to a mercury reservoir.

In order to calibrate the pyknometer, the top portion is removed and the flat flange cleaned with a *chamois* leather to remove particles of dust or mercury. The two portions are assembled, and mercury is allowed to flow into the pyknometer, filling it to the top of the capillary tube. It is left in this position for 5 minutes, to allow the temperature to reach a constant value, and finally the mercury is raised until it begins to overflow. The temperature is recorded, the tap closed and the mercury is brushed flat with the top of the capillary tube. The mercury is run into a weighed flask, the pyknometer opened and any mercury remaining is brushed into the flask by means of a camel-hair brush. Thus the volume of the pyknometer is ascertained, and this volume should give constant results with an accuracy of ± 0·005 c.c. per volume of 65 c.cs. or ± 0·008 per cent. This

figure may be used to check the accuracy of the ground-joint or the personal equation when either a new pyknometer or a new operator is introduced.

To find the bulk volume of a rock sample a similar procedure is followed, with an additional precaution. No air bubbles should be allowed to form between sample and glass. A wire is thrust down the capillary to force the sample under the mercury, and so prevent it from touching the glass when the pyknometer is being filled. A good test to observe whether air is trapped between sample and glass is to allow the sample to move inside the mercury, by tilting the filled pyknometer and observing whether the rock surface can be seen. When there are no bubbles, the mercury prevents the rock from touching the glass, and so the sample is invisible in all positions of the pyknometer.

It was necessary to filter the mercury after each determination for it gets fouled by the sample, and air bubbles then adhere tenaciously to the glass. Two batches of mercury were used, one in operation, whilst the other was distilling *in vacuo*.

Comparison.—The two methods of measuring bulk volumes differ. The micrometer measures the enveloping surface as defined by the ridges or grains on the surface, and cannot take into account any cavity smaller in area than the anvil of the instrument. Any such cavity is treated as a pore, and these constitute surface porosity. Mercury, however, can enter such indentations in the surface, although not invariably *all* indentations. A pyknometer measurement of bulk volume will, therefore, give smaller results than a micrometer method for any cylinder the surface finish of which is similar to a ground sandstone.

It must not be assumed, however, that the micrometer method is not accurate enough for porosity measurements. Porosity is not an absolute but a relative property, and therefore, however one definition of the fundamental quantities for its determination, bulk, grain and apparent volumes is varied, so will this property vary itself. None of these quantities has an absolute value. Thus the micrometer measures what may be defined as bulk volume in a particular way—viz., the smooth-surfaced ideal cylinder that has dimensions given by the average dimensions of the sample. The pyknometer measures the volume enveloped by a slightly corrugated surface as determined by the interface between mercury and sample. Both methods give accuracies of 0·2 per cent. Thus so long as one or the other method is adopted throughout a set of porosity measurements, the study of porosity as a measure of the effects of chemico-physical treatments on rocks will yield similar results. The following typical example will explain the matter.

Volumes, c.cs.		Differences in Volumes, c.cs.
Micrometer.	Pyknometer.	Micrometer-pyknometer.
17·57	17·25	0·32
17·54	17·27	0·27
17·55	17·29	0·26
17·52	17·24	0·28
17·53	17·25	0·28

The average volume for the sample by the micrometer is 17·54 c.cs. (maximum variation, 0·03 c.c. and the average volume by the pyknometer 17·26 c.cs. (maximum deviation, 0·03 c.c.). The difference between the two methods is 0·28 c.c., keeping approximately constant for all measurements. The porosity result will therefore be higher when using the micrometer for a certain apparent volume, by $\frac{0{\cdot}28}{17{\cdot}4} \times 100$ or 1·6 per cent. Assume the sample is acid-treated, then any increase in porosity resulting will be the same whether a micrometer or a pyknometer is used for bulk volume, since the surface porosity, when the sample is again ground or drilled to cylindrical shape, or the difference between the two methods, is a constant. Similarly, when comparing sands of different beds with regard to their porosities, the difference in this property of the respective beds will be the same whichever system is used as long as it is used consistently.

Grain Volume and Total Porosity.

Grain Volume.—To determine grain volume of the sample means, in effect, estimating the density of the pulverized sample, and hence the procedure followed in specific gravity or density determinations of powders and similar loose particles is suggested. The sample, after drying, was crushed to grain size, a microscope or a magnifying-glass being used to check the size of the crushed particles. A density bottle, the capacity of which was found by ordinary precision methods, was used. The fluid should preferably be an organic solvent of oils of low viscosity and density, and not water. Benzene, which has these two properties in an almost ideal form, cannot be used, however, since it is highly volatile, and thus introduces errors due to evaporation. Tetrachlorethane was found to be a suitable liquid. A known weight of the crushed material was put into the density bottle, and liquid was poured to cover the sand by approximately 10 mm. The bottle was stirred to drive out bubbles of air and put under vacuum for about 1 hour. The bottle was then filled up with the liquid, put in a thermostat for at least 2 hours to allow the fines to settle, and the temperature of the liquid was recorded just before the final weighing. The volume of the grains, the weight of which was already known, was calculated and the total porosity determined as follows :—

Let W = weight of sample the bulk volume of which is V,
w = weight of grains the volume of which is v

$$\text{volume of grains of weight } W = \frac{v}{w} \times W$$

$$\text{and total porosity per cent.} = 100 \times \frac{\left(V - \frac{v}{w} \times W\right)}{V}$$

$$= 100 \times \left(1 - \frac{vW}{Vw}\right)$$

The results obtained by repetition of this process failed to come within the limits of accuracy required by the authors for the research—viz., $\pm$ 0·25 per cent. on porosity readings. The errors could be attributed to :

(1) the fact that flotation of the fines was taking place through minute air films surrounding the finest grains. The suspended particles have an apparent density approximating to that of the liquid, and thus the apparent volume of grains shows too high a figure, (2) evaporation losses, (3) temperature changes during the operation and (4) impurity of tetrachlorethane, and consequential loss of lighter fractions and increase in the density of the fluid. Twenty-four-hour settling period would help some of these particles to come to rest, but a more effective technique was to employ " recrystallized " benzene in a modified procedure.

A special beaker, intended originally for apparent volume measurements by liquid absorption, was used. A 50-c.c. beaker equipped with a stout copper-wire handle was suspended by a fine wire tied to the middle of the handle. A small loop in the fine wire formed a fixed mark, to which the liquid level was brought when the beaker was suspended in liquid. The volume of the beaker, copper wire and fine wire up to the mark was found by immersion under liquid, and the buoyancy was noted. All determinations of this volume, with distilled water, with tetrachlorethane and with benzene at varying temperatures, and with the liquid level adjusted so that the loop was just above or just below it, agreed to $\pm$ 0·005 c.c. on an average volume of 10·2168 c.cs.—that is, $\pm$ 0·05 per cent.

The modified procedure consisted of weighing the crushed sample and the special beaker, immersed in benzene in a larger beaker, and as the benzene level was kept to a fixed mark, evaporation losses could not affect the determination of densities. The larger area facilitated the escape of air bubbles both during filling and under vacuum. From the total volume of beaker plus sand the volume of the beaker is deducted, and the grain volume is determined for the sample. The total porosity is calculated as follows :—

Assuming,

Volume of beaker (by immersion) (c.cs.)	$= V_B$
Bulk volume of sample (c.cs.)	$= V$
Weight of uncrushed sample (gms.)	$= W$
Weight of beaker in air (gms.)	$= W_1$
Weight of beaker + crushed sample in air (gms.)	$= W_2$
Weight of beaker + crushed sample in C_6H_6 (gms.) at $T°$ C.	$= W_3$
Density of benzene at $T°$ C. (gms./c.c.)	$= D$

Then Volume of crushed sample + beaker (c.cs.) $= \dfrac{W_2 - W_3}{D}$

And Volume of grains only $= \dfrac{W_2 - W_3}{D} - V_B = V_c$

Hence Total porosity per cent. $= \left(1 - \dfrac{V_c}{V} \times \dfrac{W}{W_2 - W_1}\right) \times 100.$

$$= \left[1 - \left(\frac{W_2 - W_3}{D} - V_B\right) \cdot \frac{1}{V} \cdot \frac{W}{W_2 - W_1}\right] \times 100$$

This procedure yielded repeatable results within $\pm$ 0·25 per cent.; but, as will be apparent, reproducibility of results should not be judged as a sole criterion of accuracy. If the samples were having a constant pro-

portion of fines surrounded by air films, since the conditions are rigidly fixed, then the determinations will agree remarkably well. In the case of samples the total porosities of which exceed their available porosities, the worker who obtained, say, 28·27 per cent. for total porosity as an average of three determinations with errors not exceeding $\pm$ 0·25 per cent., and 26·50 per cent. for available porosity, has no apparent reason for doubting his figures for total porosity. In the case of sands the total porosities of which are practically equal to their available porosity, any entrainment of air films around the fines in the liquid will be apparent, since the total porosity will appear paradoxically less than the available. Thus, in a typical case, a sand gave total porosities on three samples of 29·33, 29·02 and 29·41, average 29·25 per cent., and this would seem to be an accurate determination. The available porosities, within $\pm$ 0·15 per cent., as determined by liquid absorption five times on each sample using the same beaker and benzene in similar procedure, were 29·53, 29·23 and 29·61 per cent., respectively. The total porosity was in each case 0·20 per cent. less than the available; and this anomaly can only be ascribed to uncontrollable suspension of fines in the benzene by means of air film. The loss of sand on grinding is remarkably low, and the method adopted eliminates, to a great extent, errors due to this source.

In conclusion, it seems an inevitable characteristic of the procedure for finding total porosity by immersion under a liquid that certain of the fines will be suspended, thus yielding low results, although the results agree to $\pm$ 0·25 per cent. from the average. Total porosity, as explained, is not of first importance in the present investigation, since the sample is destroyed as far as any further investigation is concerned.

Apparent Volume and Available Porosity.

Liquid Absorption Method.—The principle of finding the apparent volume of a rock sample by liquid absorption methods is to saturate all available pores with some liquid of known density and to find the volume of the saturated sample by immersion in the same liquid. Thus the apparent volume, or bulk volume of rock minus the volume of available pores, is determined. The difference between bulk volume and the apparent volume is the volume of available pores.

Then, available porosity per cent. $= \left(1 - \frac{V_A}{V}\right) \times 100$

where V = bulk volume and V_A = apparent volume.

The main source of error in previous methods for determining apparent volumes by liquid absorption was the handling of the sample subsequently to saturation. Both liquid and solid material were lost.

In the present method the sample is never handled once it is in the pyknometer. Thus the weight of any particles falling from the surface of the sample will be registered in the liquid.

Tetrachlorethane was first tried, but benzene was finally chosen as the better fluid, for two main reasons: (1) an apparent loss of bulk volume by the sample, and (2) the comparative ease with which benzene can be abstracted from the sample at temperatures well below any which may

dehydrate the sample. To dry the sample of tetrachlorethane, hot air ovens had to be employed; or, if high temperatures were to be avoided, it was necessary to extract the tetrachlorethane with benzene and dry out the benzene at 22–25° C.

Evaporation losses when using benzene were completely avoided by developing the special pyknometer already described.

The sample, after its bulk volume has been found, is put in the pyknometer, and the weight of both sample and pyknometer determined. Knowing the weight of the pyknometer, the weight of the dry sample is obtained, and this figure can be used as a check on the efficiency and completeness of drying.

Benzene is poured slowly over the side of the pyknometer until the sample is covered. The pyknometer is put in a larger beaker, and the pyknometer is covered with benzene. The large beaker is placed under vacuum. Immediately bubbles will start to rise, and it is important that the apparatus is not disturbed while this initial stream of air continues (20–30 minutes), otherwise benzene tends to fill up these air channels, and it becomes more difficult to free the sample of air. The sample is then gently shaken every 5 minutes for 1 hour under an absolute pressure of 10–20 mm. of mercury. Air bubbles finally cease to emerge, and only benzene vapour bubbles arise when the sample is shaken. These bubbles are easily distinguishable by their size. By this time the benzene level is lowered by about 20 mm.; but it must not be allowed to drop below a level of about 10 mm. above the top of the sample. When evacuation is deemed complete—*i.e.*, the air remaining is negligible—air is slowly allowed to enter the vacuum chamber and the benzene is left to saturate the sample for 1 hour. Again it should be noted that the top of the sample had not been exposed to the atmosphere.

The large beaker is put on a platform over the top of a balance pan, and the pyknometer with the saturated sample inside is weighed immersed in benzene to the standard mark on the fine wire. The temperature is recorded to 0·2° C. when the weights are in equilibrium.

Then

$$\text{Volume of beaker} + \text{apparent volume of sample} = \frac{W_2 - W_3}{D} \text{ c.cs.}$$

$$\text{Apparent volume of sample, } V_A = \frac{W_2 - W_3}{D} - V_B$$

$$\text{Thus available porosity} = \left(1 - \frac{V_A}{V}\right) \times 100 \text{ (cf. above).}$$

The density of the benzene should be found for each batch used, unless it was specially purified, for different samples of "recrystallized" benzene were found to differ slightly in density.

Table IV illustrates the type of results obtained. The accuracy of finding available porosity by this method is $\pm$ 0·15 per cent., or a maximum divergence between any two results obtained of 0·30 per cent. The sample is left intact and in the same condition, with the exception of a very slight loss of weight due to loose particles from the surface (Table V), as it was before porosity determinations were commenced. Thus the method satisfies the conditions imposed on it.

TABLE IV.

Sample.	Available Porosity.					Average Available Porosity.	Maximum Deviation from Average.
	1.	2.	3.	4.	5.		
S1	29·66	29·47	29·53	29·52	29·49	29·53	± 0·13
S2	29·26	29·36	29·26	29·13	29·15	29·23	± 0·13
S3	29·66	29·50	29·67	29·63	29·61	29·61	± 0·11

TABLE V.

Sample.	Determination.	Weight of Sample.	Apparent Volume.
S1	1	33·150	12·479
	2	33·137	12·484
	3	33·125	12·474
	4	33·133	12·479
	5	33·128	12·475
S2	1	33·325	12·537
	2	33·317	12·552
	3	33·316	12·542
	4	33·309	12·548
	5	33·297	12·551
S3	1	33·033	12·441
	2	33·028	12·448
	3	33·028	12·427
	4	33·021	12·432
	5	33·021	12·433

Gas-Expansion Method.—Gas-expansion apparatus fall under two categories, both of which employ the same principles. The first type employs compressed air enclosed in a chamber, which is expanded into another to atmospheric pressure. The second type utilizes air at atmospheric pressure which is expanded to lower pressures. The high-pressure technique appears to have reached a considerable degree of accuracy in the U.S.A., but there are definite disadvantages with high-pressure technique: (1) the divergence from the gas laws, (2) subjecting the dry sample to high pressure and (3) using a steel bomb, and thus a variable volume. It was therefore decided to start with an atmospheric-pressure all-glass apparatus and to develop it to yield the accuracy required.

Preliminary Apparatus.—Tickell, Mechem and McCurdy developed what appeared to be the simplest and most straightforward apparatus. This was adopted and modified in accordance with Fig. 5.

The actual apparatus is shown in Fig. 6.

A set of aluminium cylinders, the volumes of which were accurately known, were used to calibrate and check the apparatus. The density of the aluminium cylinders was found by immersion, in distilled, boiled and cooled water, to be 2·7228, 2·7224 and 2·7223; hence an average value of 2·7225 was taken. Thus, five volumes known accurately to

± 0·005 c.cs. were used as the calibrating volumes between 34·771 and 110·156 c.cs.

The calibration of the instrument was carried out as follows: With all taps open, the mercury level was adjusted to mark (2) and the corresponding level, h_1, on the manometer was read. Tap (*b*) was closed and the mercury raised to mark (1) with tap (*d*) open. The top of the upper

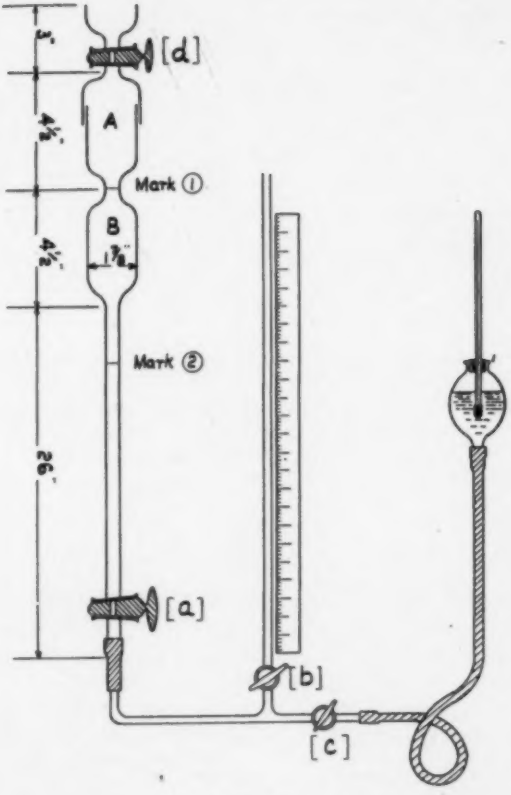

FIG. 5.

chamber was fixed in place with a thin layer of Apiezon grease of low vapour pressure. Before closing tap (*d*) the barometer was read, B_{P_1}, and the air inside *A* was allowed to attain equilibrium with the surrounding air. Tap (*d*) was closed and the mercury allowed to flow back, the air in *A* expanding into chamber *B*. Tap (*b*) was then opened, and when the level of mercury reached mark (2), the level in the manometer h_2 was finally read.

Air was then admitted through tap (*d*), the top part removed, a standard volume introduced in *A* and the procedure repeated. Thus

Volume of specimen	v
Volume of chamber *A*	V_1
Volume of chamber *B*	V_2
Barometric pressure with blank	B_{P1}
Difference between h_2 and h_1 with blank . .	H_1
Barometric pressure with v in *A* . . .	B_{P2}
Difference between h_2 and h_1 with v in *A* . .	H_2

Then, for the blank test

$$B_{P1}V_1 = (B_{P1} - H_1)(V_1 + V_2) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

or

$$V_1 = \left(\frac{B_{P1}}{H_1} - 1\right)V_2$$

And from the test with v

$$B_{P2}(V_1 - v) = (B_{P2} - H_2)(V_1 + V_2 - v) \quad . \quad . \quad . \quad (2)$$

or

$$v = V_1 - V_2\left(\frac{B_{P2}}{H_2} - 1\right)$$

From equations (1) and (2), the two unknown values V_1 and V_2 were calculated.

The volume of a rock sample was found by placing it in chamber *A* and repeating the operation outlined above. Then, from the barometric pressure *B*, the mercury head *H*, and the values of V_1 and V_2, the volume of the sample was calculated according to the formula

$$v = V_1 - V_2\frac{(B - H)}{H}.$$

This apparatus yielded erratic results. Table VI gives the values of V_1 and V_2 obtained by calibrating with different volumes and on different days.

TABLE VI.

Calibrating Volume.	Volume V_1.	Volume V_2.
B_1 = 34·7713	192·63	177·14
B_2 = 51·9296	195·73	200·00
B_3 = 73·1997	190·95	177·07
B_3 = 73·1997	194·03	180·43
B_4 = 92·7380	192·35	177·13
B_5 = 110·1564	191·41	176·25
Average	192·85	181·33

Similarly, the accuracy obtained by measuring the volume of the aluminium cylinders in the apparatus was shown to be inexact. Typical results are shown in Table VII.

FIG. 1.

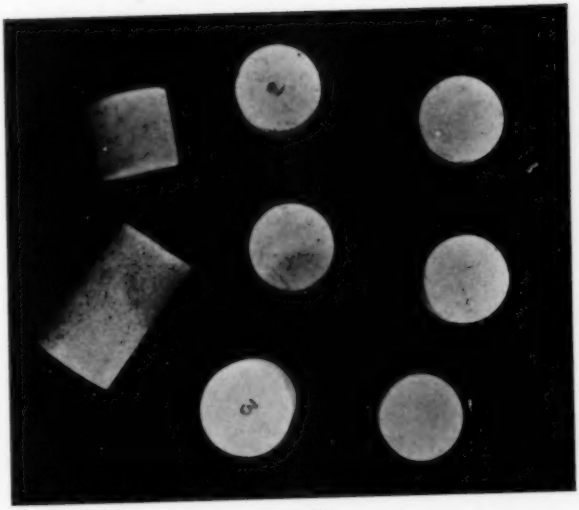

FIG. 2.

[*To face p.* 382.

FIG. 3.

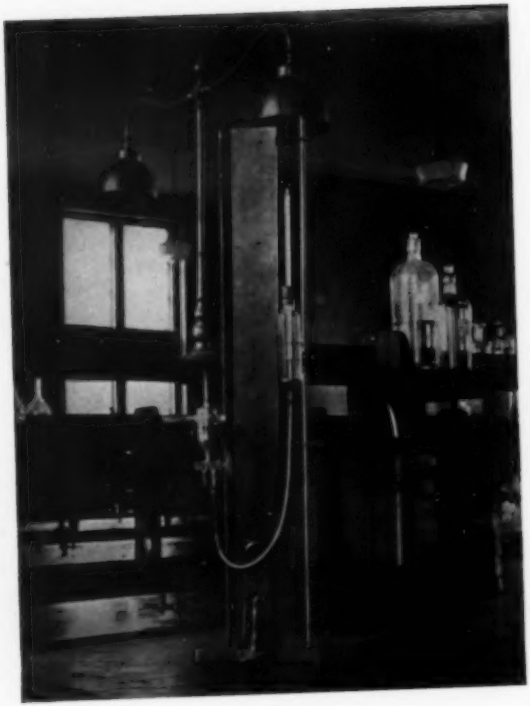

FIG. 4.

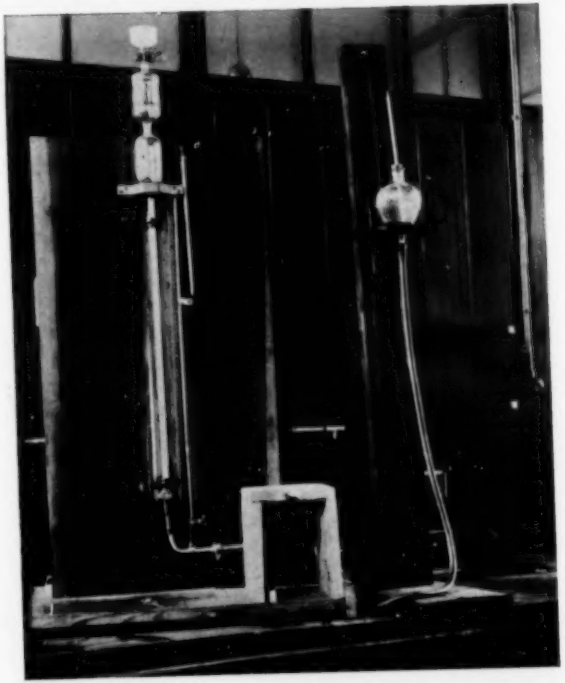

FIG. 6.

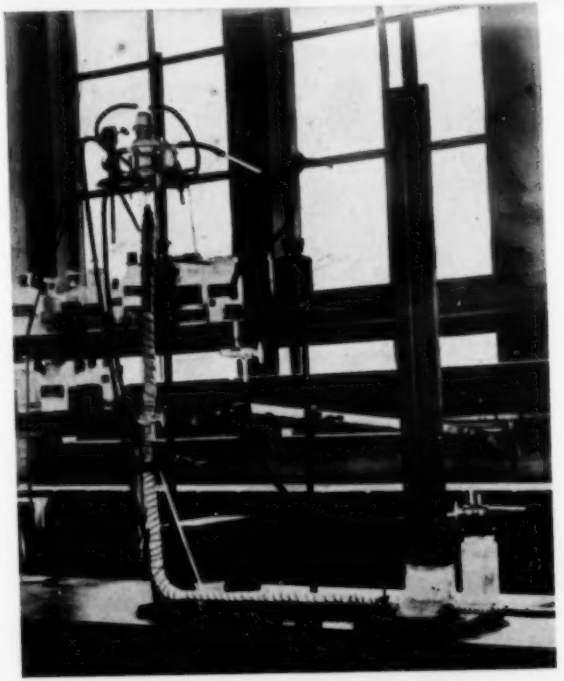

FIG. 7.

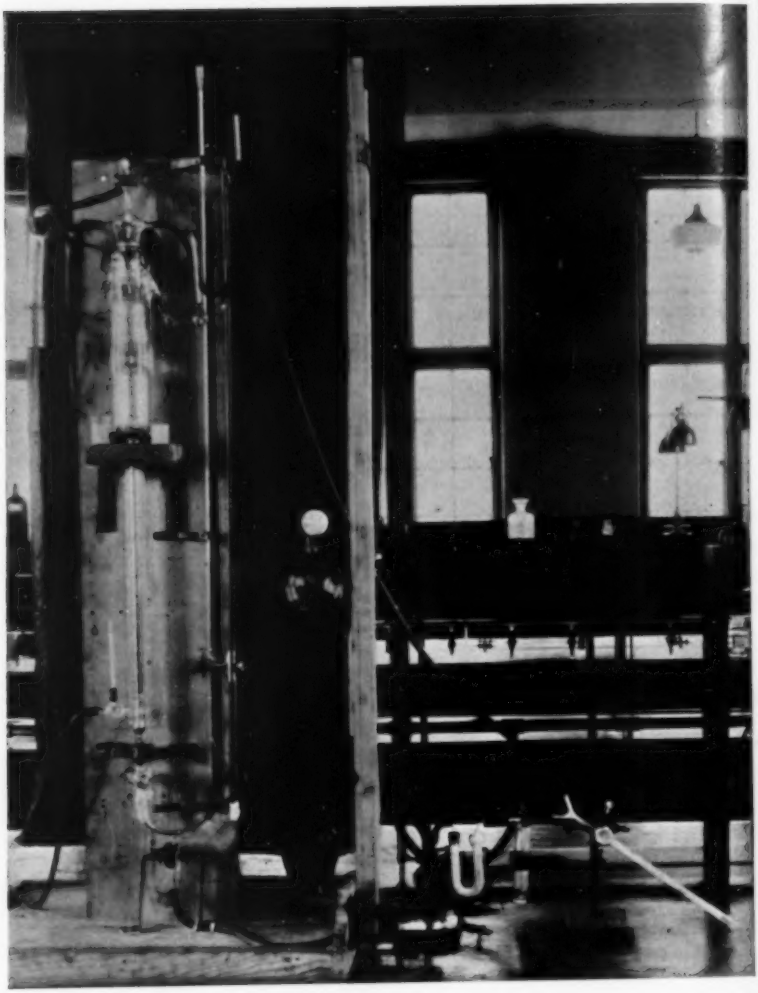

FIG. 8.

TABLE VII.

Calibrating Volume.	Percentage Error on Volume Measured.				
	B_1.	B_2.	B_3.	B_4.	B_5.
B_5 = 110·16	+ 0·43	+ 0·63	− 0·71	+ 0·59	—
B_4 = 92·74	− 1·19	− 0·74	− 0·36	—	− 0·87
B_3 = 73·20	− 0·11 + 1·40	− 0·02 + 0·49	— —	+ 0·06 − 0·60	− 0·55 + 0·88
B_2 = 51·93	− 0·09 − 1·60	— —	+ 0·04 − 0·52	+ 0·09 + 0·74	− 0·51 − 2·02
B_1 = 35·77	— —	+ 0·07 + 1·58	+ 0·11 + 1·05	+ 0·15 + 0·61	− 0·44 − 0·41

Average figures for V_1 and V_2 were then taken from six determinations with different calibrating volumes, $V_1 = 191{\cdot}89$ and $V_2 = 177{\cdot}10$, and tests on the accuracy of measuring the volumes of the cylinders were again conducted with the following results.

TABLE VIII.

Case.	Percentage Error on Measured Volume.				
	B_1.	B_2.	B_3.	B_4.	B_5.
1	− 1·24	− 0·93	− 0·67	− 0·89	—
2	+ 0·88	+ 0·40	+ 0·25	+ 0·01	—
3	+ 1·61	+ 2·45	+ 1·49	+ 2·50	− 0·36

From the theory governing the apparatus, the smaller the volume of v—*i.e.*, the volume measured—the larger the error. Hence the blank determination—*i.e.*, when $v = 0$—must produce the maximum discrepancies. This theory was tested by calibrating with two large volumes instead of the method already outlined. Thus the two formulae, using two known volumes v_1 and v_2, are correct, and will give the values for V_1 and V_2 :—

$$v_1 = V_1 - V_2\frac{(B_1 - H_1)}{H_1}$$

$$v_2 = V_1 - V_2\frac{(B_2 - H_2)}{H_2}$$

Using $v_1 = 92{\cdot}7380$ c.cs. and $v_2 = 73{\cdot}1997$, the values for V_1 and V_2 were found to be 192·74 and 177·62, respectively. This calibration was checked by measuring the volumes of B_5 (110·16), B_2 (51·93) and B_1 (34·77). The percentage errors were − 0·63, + 0·04 and + 0·11, respectively, or a maximum of 0·7 c.c., against a maximum of 2·3 c.cs. when using a blank determination. Nevertheless, the errors were still excessive.

Modified Intermediate Instrument.—These instruments are in the form of air thermometers, and hence are very sensitive to temperature change. A small water-jacketed instrument was therefore made with three additional features (Fig. 7). A tap was fitted to the insulated vertical tube below the chambers, to facilitate calibrating the lower chamber accurately with mercury, and the volume of this chamber was determined to within $\pm$ 0·005 c.c. The volume of the upper chamber was then found using different cylinders in the normal manner to an accuracy of $\pm$ 0·1 c.c. Another feature was that the tap in the upper chamber was connected to an air-pump and a drying tube containing soda lime and calcium chloride. Dry air, free from CO_2, was therefore used, since water vapour and carbon dioxide do not obey the gas laws accurately. The top of the original apparatus was fitted with a greased ground joint, and this may have contributed to the discrepancies. In the tentative apparatus a conical ground joint, accurately ground so that no grease was required to hold the vacuum was incorporated. The flat flanges, however, were greased after fixing the cap.

With such additional precautions, different volumes were measured with the following accuracies :—

Volume Measured.	19.	16.	14.	11.	8.	5.
Error in c.cs. . . .	— 0·02 — 0·05	— — 0·06	0·02 —	— 0·28 — 0·38	— 0·38 — 0·44	— 0·42 —

Final Apparatus.—In designing the final form, temperature, pressure, fluid medium and apparatus were placed under rigid control to ensure the accuracy required.

The temperature of the mercury and air was governed by water-jacketing the whole of the left limb of the apparatus, including the cap, and two thermometers (calibrated, reading to 0·2° C.) were placed at entry and exit of the water for recording any temperature changes. The water from the tap did not vary more than 0·5° C. during 1 hour. To stabilize the temperature of the apparatus a third chamber was introduced below the second chamber. The mercury in this chamber acted as a thermal reservoir when expansion took place and when the upper two chambers, filled with air and sample only, were very susceptible to thermal changes. It was not necessary to water-jacket the manometer.

In considering the pressure, the manometer was made of the same diameter as the capillary constrictions between the chambers, and errors due to the meniscus of mercury in the two limbs of the apparatus were avoided. In every determination of volumes the barometric pressure as well as the pressure drop on expansion were read. The apparatus was designed to be used as a barometer, if necessary. The glass manometer tube was graduated in mms., and a telescope with light was used to read the pressure heads.

Air is composed mainly of true gases, but has water vapour and carbon dioxide (below critical temperatures) in small but appreciable quantities, and these were removed. It was found advantageous, for keeping the mercury clean in the manometer and reservoir, to place drying tubes in the inlets. The mercury was triple distilled. No grease was used except where absolutely essential (taps) and then only in minimum amounts.

In designing the apparatus, the formula for calculating volumes was investigated,

$$v = V_1 - V_2\frac{(B-H)}{H}$$

Any error in calibrating the volume, V_1, will be directly transferred to v, whilst errors in V_2 will be multiplied by a fraction. Again the method of calibration must be the same for V_1 and V_2, so that if the method tends to give too high or too low values, both V_1 and V_2 will have errors in the same direction, and, therefore, v will have the difference in errors. Hence V_1 must be mercury calibrated in the same way as V_2, and since the pyknometer (Fig. 4) has proved an accurate chamber for calibration and for keeping its volume constant, this was incorporated. Thus the upper chamber of the apparatus was exactly the same as the pyknometer, except that it was water-jacketed. The flat joint was accurately ground, and with the edges, *but not the flanges*, greased, this joint was found to hold a Torricelli's vacuum for periods of over 24 hours. Instead of the flat springs used with the pyknometer, helical springs were employed to keep the upper and lower portions of the upper chamber in position. (Fig. 8.)

It will be noticed that in all previous atmospheric pressure-vacuum apparatus the two chambers were made equal in capacity. That this procedure is not the best to follow will be apparent from two considerations :—

1. In the formula $v = V_1 - V_2\frac{(B-H)}{H}$, air is assumed to follow isothermal expansion, or the index in the general gas formula

$$P_1V_1^n = P_2V_2^n$$

is assumed to be unity. Should the index not be unity, but some value slightly higher, an error will be introduced in v. A new formula is derived,

$$\begin{aligned}
&B(V_1-v)^n = (B-H)(V_1+V_2-v)^n\\
\text{Let}\quad &V_1+V_2 = kV_1\\
&B(V_1-v)^n = (B-H)(kV_1-v)^n\\
&H(kV_1-v)^n = B[(kV_1-v)^n-(V_1-v)^n]\\
&\frac{H}{B}\Big[(kV_1)^n - {}^nC_1(kV_1)^{n-1}v + {}^nC_2(kV_1)^{n-2}v^2\ldots\Big]\\
&\qquad = \{[(kV_1)^n - {}^nC_1(kV_1)^{n-1}v + {}^nC_2(kV_1)^{n-2}v^2\ldots]\\
&\qquad\quad - [V_1^n - {}^nC_1(V_1)^{n-1}v + {}^nC_2(V_1)^{n-2}v^2\ldots]\}\\
&= [V_1^n(k^n-1) - {}^nC_1V_1^{n-1}v(k^{n-1}-1) + {}^nC_2V_1^{n-2}v^2(k^{n-2}-1)\ldots]\\
&V_1^n\Big[k^n\Big(\frac{H}{B}-1\Big)+1\Big] - {}^nC_1V_1^{n-1}v\Big[k^{n-1}\Big(\frac{H}{B}-1\Big)+1\Big]\\
&\qquad + {}^nC_2V_1^{n-2}v^2\Big[k^{n-2}\Big(\frac{H}{B}-1\Big)+1\Big]\ldots = 0
\end{aligned}$$

The value of n cannot exceed 1·4 as a limit, and is in actuality very nearly unity. The value of k is between 2 and, say, 10, which, for ease of manipulation, may be taken as an upper limit. For the purposes of this discussion assuming $k = 2$ and $n = 1{\cdot}2$, the three terms of the equation above

are equated for a value of $v = \frac{1}{2}V_1$. Then $\frac{H}{B} = 0{\cdot}73$ from the polytropic equation and,

$$\text{first term} = 0{\cdot}38V_1^{1{\cdot}2}$$
$$\text{second term} = 0{\cdot}41V_1^{1{\cdot}2}$$

Therefore third + all other terms $= 0{\cdot}03V_1^{1{\cdot}2}$
Since $0{\cdot}38V_1^{1{\cdot}2} - 0{\cdot}41V_1^{1{\cdot}2} + \epsilon = 0$
Thus, neglecting all terms beyond the second,

$$V_1^n\left[k^n\left(\frac{H}{B}-1\right)+1\right] = {}^nC_1V_1^{n-1}v\left[k^{n-1}\left(\frac{H}{B}-1\right)+1\right]$$

or
$$v = \frac{V_1^n\left[k^n\left(\frac{H}{B}-1\right)+1\right]}{{}^nC_1V_1^{n-1}\left[k^{n-1}\left(\frac{H}{B}-1\right)+1\right]}$$

$$v = \frac{V_1\left[k^n\left(\frac{H}{B}-1\right)+1\right]}{n\left[k^{n-1}\left(\frac{H}{B}-1\right)+1\right]}$$

or, when $n = 1$

$$v = V_1\frac{k\left(\frac{H}{B}-1\right)+1}{\left(\frac{H}{B}-1\right)+1}$$

or
$$v = V_1 - V_2\frac{(B-H)}{H}$$

which is the isothermal equation. Thus the expression is substantially true for low values of n.

The important fact emerges, however, that for a first approximation, whatever the value of n,

$$v = \phi\left(-\frac{B}{H}\right)$$

as will be evident by simplifying the fraction.
Thus let δ = error introduced in v due to taking $n = 1$ while actually n is higher than 1.

P_1 = initial pressure in V_1
P_2 = Final pressure in $V_1 + V_2 - v$

$$\delta = \phi\left(-\frac{B}{H}\right) = \phi\left(-\frac{P_1}{P_1-P_2}\right) = \phi\left(\frac{P_1}{P_2-P_1}\right)$$

$$\frac{1}{\delta} = \phi\left(\frac{P_2}{P_1}-1\right)$$

$\frac{P_2}{P_1}$ is always a fraction. Thus as $\frac{P_2}{P_1}$ increases, $\frac{1}{\delta}$ decreases, *i.e.*, δ increases. This fact can be interpreted in two ways :—

(i) As the volume to be measured, v, gets smaller the error gets larger; expansion is not high, therefore $\frac{P_2}{P_1}$ is large.

(ii) For a given volume to be measured, v, the larger the volume of the second chamber, the greater the expansion and consequently the smaller the error since $\frac{P_2}{P_1}$ gives a small value.

2. Another advantage gained by making the volume V_2 as large as possible is that at low pressures van der Waal's equation and Boyle's Law are the same. Thus with higher expansion ratios Boyle's Law applies more strictly to the pressure–volume relationship of the air inside the apparatus.

With the high-pressure types of porosimeters, it is found that the higher the pressure in the steel bomb the more accurate is the result. In other words, the larger the expansion of the gas, the more accurate the procedure.

These considerations suggested a deviation from the accepted principle of making both chambers equal in volume. An upper limit exists, however, since the column will be highly stressed by the mercury it is supporting. Thus, it was concluded that for an upper chamber, the cylindrical portion of which was 35 × 50 mms., a lower chamber the main dimensions of which were 50 × 80 mm. was sufficient. The pressure reached with a volume of 20 c.cs. would be about 150 mms. Hg, whilst for 40 c.cs. it would reach 100 mms. approximately.

Details to be observed in the design of the apparatus may be mentioned. At the bottom of the column the two-way tap connects the column to the manometer tube through a wide-bore tube, but the connection to the atmosphere is through a narrow capillary fitted with a V-groove for finer adjustments in the calibration of the instrument. The T-piece between manometer and column should slope upwards, as air bubbles would collect in a horizontal T-piece. A plumb-bob is fixed to the board to align both column and manometer in vertical planes, and three adjusting screws, fixed to the base, facilitate this operation.

Before any tests were made, the apparatus was subjected to a rigorous cleaning process to eliminate the presence of any high-tension vapour. The apparatus was dried by applying suction at the top of the upper chamber and manometer, whilst allowing air to enter through the reservoir *via* a Dreschel bottle containing concentrated sulphuric acid, and subsequently through cotton wool. To eliminate dust all samples were put in the apparatus in a thin glass cylinder of known volume.

To calibrate V_1 and V_2 the cap was taken off the apparatus and the ground joint cleaned with leather to remove loose particles. The cap was placed in position, and after the springs were fixed, grease was applied in an unbroken ring around the edge (not on the flange). With the mercury level at the bottom of the column, all taps were opened connecting the inside of the apparatus to the vacuum pump. The water was allowed to circulate in the jacket. The water pump was opened sucking the mer-

cury up the column to a maximum level—just below the upper chamber. (The mercury permitted of no bubbles remaining on the glass with this procedure, whilst filling the chambers by simply raising the reservoir resulted in air bubbles persisting on the glass.) The upper chamber was evacuated by gently raising the mercury to a point just above the uppermost tap (Fig. 8). This tap was closed, the mercury level lowered below the ground joint, and any residue of air expelled by repeating the process three or four times. The peculiar metallic sound made by the mercury on impact with the closed glass tap denoted completeness of evacuation. The mercury was allowed to reach the temperature of the water, the maximum difference between the two thermometers being not more than 0·2° C., the mercury was run through the two-way tap into a weighed flask and the volume of V_1 was found. It is advisable that the uppermost tap remains closed. If air is allowed to follow the mercury on running out, globules remain adhering to the glass at the joint. The lower chamber, however, can be calibrated while connected to the atmosphere. Table IX gives the calibration. The breaks in the columns denote the position where the cap was removed, the flange cleaned, and the tap refixed and greased to find whether such procedure affected the volume. Where the average of two figures was taken, one figure was obtained by successive weighings of small quantities of mercury, whilst the other was obtained by weighing all the mercury in the chamber at once.

TABLE IX.

V_1.		V_2.	
Measurement.	Average.	Measurement.	Average.
64·14 64·16	64·15	175·18 175·15	175·17
64·13	64·13	175·11	175·11
64·21 64·09	64·15	175·12 175·07	175·10
Final Average	64·14 c.cs.		175·12 c.cs.

The apparatus was then used as a barometer for a number of days to check the accuracy of the ground joint and to see whether the expensive barometer could be eliminated. The level of the upper mark M_1 was determined on the manometer, the apparatus was evacuated and the residue of air was pumped out as in the procedure adopted for calibration. The uppermost tap was closed, the mercury was lowered until the level in the apparatus was at the upper mark, and the manometer read, h. Then the apparent barometric pressure,

$$B_A = h - M_1.$$

Barometric reading . .	756·9	757·27	757·40	759·25	759·54	760·00	760·25
$h - M_1$	756·7	757·6	757·5	759·1	759·2	759·8	760·7

The error is $\pm$ 0·45 mm. This figure can be substituted in the formula

$$v = V_1 - V_2\frac{(B - H)}{H}$$

and the errors due to the discrepancy can be calculated for different values of H. For values of H between 580 and 670 (v, between 12 and 40 c.cs. approximately), the errors in v, will be between 0·14 and 0·12 c.cs. respectively. In actual experiments the errors are less than 0·10; those introduced by other factors appear to counteract this one. For precise work, however, a barometer is essential.

To measure the apparent volume by this apparatus, the following procedure was adopted :—

(1) The cap was opened, the flange cleaned, the sample in its glass envelope was placed in the upper chamber, the top was fixed with the springs and the edge of the flange greased.

(2) The reservoir was lowered to its lowest point, all taps connecting reservoir, manometer and apparatus were opened, connecting vacuum pump to the inside of the chamber.

(3) Water was circulated in the water-jacket.

(4) The air, the sample and the inside of the apparatus were dried by applying suction, evacuating apparatus and allowing the mercury to rise to a fixed point in V_2, then admitting air again through $CaCl_2$ and soda-lime tubes. This procedure was followed ten times.

(5) The level of the lower mark, below V_2, was read on manometer (M_2).

(6) Suction was applied until mercury was just below the upper mark, when the upper tap was closed.

(7) The tap between the reservoir and the instrument was closed.

(8) The three-way tap between pump and drying-tube was opened, thus shutting off the vacuum pump from the instrument and connecting the instrument to atmosphere.

(9) The upper tap was opened, permitting the upper chamber to be filled with dry air at atmospheric pressure.

(10) The reservoir was raised to the level of the upper mark.

(11) The tap between reservoir and apparatus was opened, and the mercury was brought to the mark and the tap was then closed.

(12) The barometric pressure was read (B).

(13) When the difference in the thermometer readings did not exceed 0·2° C., the upper tap was closed and the average temperature reading of the two thermometers was recorded (t_1).

(14) The mercury was lowered by lowering the reservoir and opening the lower tap until it reached the lower mark.

(15) Temperature and mercury level in the manometer were read (t_2 and h).

(16) Opening the upper tap the sample was free to be taken out.

If the temperature did not vary, then the volume of the sample plus envelope was calculated from

$$v = V_1 - V_2\frac{(B - H)}{H}$$

where V_1 = volume of the upper chamber (c.cs.), V_2 = volume of the lower chamber (c.cs.), B = barometric pressure (mm. Hg.), $H = h - M_2$ (mms. Hg.), v = volume of enclosed solid.

If the temperature changed during the operation, H' was substituted for H in the equation, where

$$B - H' = \frac{(B - H)(t_1 + 273{\cdot}1)}{t_2 + 273{\cdot}1}$$

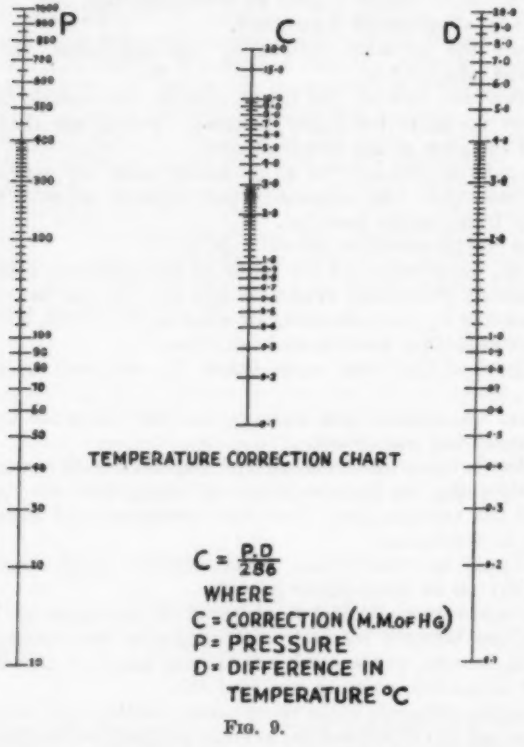

FIG. 9.

A nomograph, however, was constructed to find the correction to be added or subtracted to the value $(B - H)$ to give $(B - H')$ accordingly as the temperature decreased or increased. Fig. 9 is self-explanatory. A line connecting the temperature difference, D, and the pressure, $P = (B - H)$, will intersect the C or correction axis at the required value.

Table X gives the results obtained on aluminium cylinders the volumes of which were determined by immersion methods. It is evident that the drying procedure as described is necessary and sufficient.

Thus the instrument measures volumes to within $\pm$ 0·05 c.c. From this figure and the errors for bulk volume measurement ($\pm$ 0·03 c.c.), the

TABLE X.

Sample.	Wet. Volume, c.c.	Wet. Error, c.c.	Dry. Error, c.c.
N_1	12·32	− 0·15	− 0·03
N_2	19·33	− 0·19	− 0·01
N_2	19·33	− 0·12	− 0·03
N_3	25·88	—	+ 0·03
N_3	25·88	—	+ 0·05
$N_1 + N_3$	31·65	− 0·20	+ 0·05
$N_1 + N_2$	38·20	− 0·50	+ 0·05
$N_1 + N_2$	38·20	− 0·17	− 0·04

accuracy of the method can be calculated. The maximum error occurs when the bulk measurement is + 0·03 c.c. and the apparent volume − 0·05 c.c. in error, or *vice versa*. Thus an error of 0·08 c.c. will result in the volume of the voids. The other extreme will be 0·08 c.c. in the opposite direction. Thus the maximum divergence in volume of voids as measured by these methods will be 0·16 c.c., and to obtain an accuracy ± 0·25 per cent. the bulk volume must be 32 c.cs.—a maximum divergence of 0·5 per cent. With larger bulk volumes the error is smaller; with smaller volumes the errors are correspondingly higher.

Finally, Table XI is given to illustrate the actual repeatability of available porosity measurement using the gas-expansion porosimeter on a sample the bulk volume (32 c.cs.) of which has been calculated to give a maximum deviation of 0·50 per cent. It will be seen that the error is actually one half the calculated, and this is the usual case, since in the calculations the worst was investigated, whilst the experimental errors tend to annul each other, following the law of averages.

TABLE XI.

	I.	II.	III.	IV.	V.
Height, cms.	5·0713	5·0709	5·0699	5·0694	5·0708
Diameter, cms.	2·8695	2·8697	2·8684	2·8684	2·8649
Bulk volume, c.cs.	32·80	32·80	32·76	32·76	32·69
Barometer	763·13	763·05	763·00	762·45	762·23
H	627·05	626·85	626·80	626·15	625·80
Apparent volume, c.cs. (Sample + glass)	26·12	26·09	26·09	26·02	25·96
Volume of glass	2·59	2·59	2·59	2·59	2·59
Apparent volume sample, c.cs.	23·53	23·50	23·50	23·43	23·37
Volume of voids, c.cs.	9·27	9·30	9·26	9·33	9·32
Available porosity, per cent.	28·27	28·36	28·33	28·48	28·51
Average porosity—Actual porosity	+ 0·12	+ 0·03	+ 0·06	− 0·09	− 0·12

Conclusions.—Both liquid absorption and gas-expansion methods have been developed for measuring the available porosities of rocks with a maximum error of ± 0·25 per cent. from a mean value. Actual results

obtained, in both cases, are nearly twice as accurate. Of the two processes, the gas-expansion method is quicker, since in repetition work on any particular sample no drying period is necessary, as is the case with the liquid-absorption method.

Total porosity determination is not recommended as an accurate measure of physical and chemical treatments of rocks, although a method has been developed to determine total porosity with accuracy.

Oil Engineering & Refining Department,
University of Birmingham.

THE CHEMISTRY OF PETROLEUM—PAST AND PRESENT.*

By Professor Dr. J. von Braun, Heidelberg.

It was maintained many years ago by the physicist C. Neumann that the discovery of something new was in itself a great delight and the purest joy. Unfortunately it cannot be denied that there are few men who find such satisfaction in the discovery for their own sake of new facts, of hitherto unnoticed relations, or of previously unknown laws, and who thus subscribe to Neumann's classical dictum. The discovery of something new is in itself not sufficiently fascinating for the great majority; their interest is only aroused if there is a practical use for this new thing, if an industrial application results from it with an improvement in one direction or another of our standard of living. So it happens that substances or groups of substances produced by Nature often remain for a long time more or less completely unnoticed by the great majority. These substances suddenly gain interest when it is found that they have some practical application; they are examined in greater detail, their character is probed and they are transformed artificially and purified in order to make them still more suitable for industrial purposes.

Such a substance—or more exactly, group of substances—is petroleum. This remarkable organic liquid which oozes from the ground in divers places has indeed been known for a considerable time. For a long time it has had a limited use on account of its combustibility and the luminosity of its flame, and it was also used for medicinal and similar purposes; but all this was only to an extremely limited extent. The quantity available would in itself have been amply sufficient to investigate its constitution, its properties and its possible chemical transformations, as has been done with so many natural substances since the days of Lavoisier and Scheele. This did not happen, however, with petroleum, the main reason being probably that the small quantity available to mankind did not justify greater interest.

All this was changed very suddenly about eighty years ago, when the art of man came to the aid of Nature, and drilling made enormous quantities of petroleum immediately accessible. There then followed an extension of the technical applications of petroleum in many directions, and at the same time, greatly stimulated by economic considerations, there began an intense scientific investigation of this valuable material which had been given so suddenly to mankind.

We are still in the middle of this technical development, and there is as yet no suggestion of concluding it. We are far from any degree of completeness in our investigations, even such as is shown to quite a large extent by the research into the alkaloids and sugars, two fields which have been worked on for many years so successfully here at the University of

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Hamburg. It appears attractive in spite of this to review the progress made, and to bring oneself up to date as regards the most important problems which it has been possible to solve during the past eighty years, and to see which are the most important and attractive for future investigation.

Petroleum, as it leaves the earth, consists of a mixture of a very large number of compounds of carbon and hydrogen and also small amounts of substances containing oxygen, sulphur and nitrogen. The complete investigation and elucidation of the nature of such a mixture from a purely chemical and technical viewpoint would require answers to the following three questions:

1. What are the constituents of petroleum; how can each one be identified and separated sharply from the others? What is the constitution of each of these constituents, or at least, to what class of compounds does it belong?

2. What is the physical and chemical behaviour of each constituent; what reactions will it undergo?

3. How can new technical applications for petroleum products be devised from a knowledge of the behaviour of its constituents, and can the older accidentally discovered uses be materially improved by application of such knowledge?

In what follows I shall endeavour to show how far the development of petroleum has answered these three questions since the interest in petroleum became so much greater, and, in particular, what fundamentally new viewpoints are now of importance in the treatment of the three questions.

I should like to observe, first of all, that the sharp separation of the individual components of petroleum and an exact knowledge of all details of their structure (Question 1) are furthest from completion; we have much more that is new to record about the possible reactions of the constituents of petroleum (Question 2) and about the improvements in the technical application of the results of this knowledge (Question 3).

The advances in the realm of the reactions of the constituents of petroleum are due to advances not only in preparative chemistry but also in physical chemistry; to new methods and to the application of kinetic, thermodynamic and electronic theories; also, on the other hand, discoveries in the domain of petroleum have had their reflections in general chemistry and have given impetus to new developments.

These advances have also increased our knowledge of the origin of petroleum in Nature. Chemical conclusions and considerations have supplemented the work of the geologists in a very gratifying way.

I. The Identification and Isolation in a Pure State of the Individual Constituents of Petroleum.

We know now, as I shall show later, that natural petroleum contains three kinds of hydrocarbons: paraffins, aromatic hydrocarbons and the richer in hydrogen alicyclic hydrocarbons, in particular, derivatives of *cyclo*pentane and *cyclo*hexane. In addition to these, it contains (*a*) oxygen-containing naphthenic acids and oxygen-containing parent substances of the phenols, of unknown nature, and (*b*) more complicated substances of

unknown nature containing sulphur and nitrogen. Comparing this with that which was known some sixty to eighty years ago, when first the scientific investigation of petroleum was begun, we notice two particular points in connection with the hydrocarbons:

(1) Sixty to eighty years ago, a further, fourth class of hydrocarbons was believed to be a constituent of petroleum—namely, the olefines.

(2) The presence of compounds of *cyclo*pentane and of *cyclo*hexane was unknown.

The reason for this latter is very simple: this type of compound—the alicyclic hydrocarbon—was still unknown. It was discovered about 1880 by almost contemporaneous work in three directions: reduction of aromatic hydrocarbons by Baeyer, the elucidation of the structure of the terpenes by Wallach, and—which interests us most—by investigation of petroleum, an investigation with which are linked the names of Beilstein and Markownikow. The chemistry of petroleum is thus closely associated with this exceedingly important branch of organic chemistry, which in little more than half a century has expanded and developed into one of its finest sections.

Separation by Fractional Distillation.

The early assumption that olefines were present in natural petroleum—an assumption which is nowadays discredited—has a very important explanation which was only gradually realized. In order to achieve a more or less complete separation of petroleum into individual components, it was submitted to fractional distillation. This represents one of the four simple methods (which will be described immediately) of separating mixtures of liquids such as occur in petroleum, and would present no further complications if the petroleum were to an appreciable extent thermostable. It was gradually recognized, however, that this was not the case. The sulphur and nitrogen compounds are completely broken up on distillation and are altered beyond recognition, the former yielding sulphur, hydrogen sulphide, mercaptans, sulphides, thiophenes and thiophanes, and the latter, which in their original form are not basic, giving rise to basic compounds of lower molecular weight, so that at the present time we have no conception of what sulphur- and nitrogen-containing constituents are present in native petroleum. To discover this will be a most important task for the future, though it may not be an easy one. Whilst the relations appear to be much the same with the oxygen-containing compounds in petroleum which yield phenols, it is important that the naphthenic acids behave differently: they survive distillation to a large degree without considerable change, as is shown by my own experiments (which I shall deal with later). The principal constituents of petroleum—the hydrocarbons—also suffer some decomposition during distillation, being decomposed more and more as the molecular weight increases. I propose to go further into the nature of this change (as we see it to-day), and should like to remark here that (*a*) olefines, which were not originally present, arise from these changes, and (*b*) a definite though not complete reduction in the extent of this decomposition can be brought about by distillation at low pressures. This method of working,

which has in recent times been so widely developed even in large-scale practice, has allowed of a considerable reduction in the decomposition of the petroleum during distillation. The new refinements, such as those of Villard and of von Hevesy, permit us to expect many improvements in the future, at least in scientific work.

Separation by Cooling.

The second method of separation of liquid and also of gaseous mixtures, which is directly opposed to that of distillation, is the application of cooling. This has been in use in one connection for many years in the separation from petroleum of a part of its components—namely, the isolation of the mixture of solid high-molecular hydrocarbons of the methane series which are known as paraffin waxes. Nothing fundamentally new has arisen in this field since the beginning of real petroleum chemistry about the middle of the last century. In the last few decades, however, the development of refrigeration technique has made it possible, by means of more or less intensive, more or less graded cooling, to separate individual components from the easily volatile constituents dissolved in petroleum, some of which are gaseous at ordinary temperatures. Thus, for example, it has been possible to obtain propane, butane, propylene, butylene, etc., in a pure state and to place these in unlimited quantities at the disposal of the chemists for further development, as I shall describe later.

Separation by Selective Solubility.

A third method of separating the constituents of petroleum, which holds considerable possibilities for the future, is the application of selective solubility. It is remarkable that use has not been made of this before. Aisinmann towards the end of the last century and Charitsckow at the beginning of this century were the first to use the method. They found that such media as ethyl and amyl alcohol respectively could be used for separating petroleum into fractions of lower and higher specific gravity, although the nature of these was not further determined. About 1910 these processes were followed by the famous method of Edeleanu, which made use of liquid sulphur dioxide, a medium which until then had rarely been used for solvent purposes. It was found that this solvent dissolves the aromatic and unsaturated components more easily than the paraffins and alicyclic components, and thus allows the removal of the latter from any given oil. Unfortunately it does not go so far as to allow the oil to be split into narrow fractions of graded solubility and uniform composition, nor can this be done with the many materials which have been used later in following up Edeleanu's work, materials the number of which are still increasing, such as phenol and the cresols, furfurol, dichlordiethyl ether, propane, etc., which serve perhaps technical but not scientific purposes. A process worked out a short time ago by means of which it may be possible to advance a few steps further is that of von Pilat. If the resinous, high-molecular asphaltic components of petroleum are precipitated by means of light-boiling benzine and then methane is forced in under pressure, a series of fractions are precipitated which are first viscous and then become more and more mobile as the molecular weight decreases. These highly

interesting experiments are still in progress. It is hoped that they will be successful at least for scientific work, and that they will allow of petroleum fractions being obtained which have a short boiling range and consist of only a few individual components which have not been partly decomposed by distillation. Petroleum fractions should thus become available for examination in an unchanged condition.

Separation by Adsorption.

The fourth method of separating the constituents of petroleum is half physical, half chemical in character—namely, the method of adsorption. This has, however, had but little success. It was used decades ago in a purely empirical manner in order to remove coloured and asphaltic materials from petroleum by treatment with charcoal or with hydrosilicates such as Florida-earth. Since then the principles of adsorption have become better understood, and we know now that chemical forces come into play during adsorption, arising both from the adsorbent and from the adsorbed materials, and that therefore, of the hydrocarbons, the unsaturated and aromatic ones are adsorbed more than the paraffins and alicyclics. It has been proved that petroleum can be separated into fractions of varying density, boiling point and viscosity by filtration through fine-pored media, but little advance has been made beyond this point, and our ultimate object, the separation of pure individual compounds, has not yet been attained in this way. I feel, however, that we do not need to look too pessimistically into the future. The technique of adsorption, or as it is now termed where colours are concerned, "Chromatography," has made very great progress in recent times; it has become so much improved that very similar compounds of, for instance, the carotin family can be separated from each other in this way. It seems to me by no means impossible that this technique may also be successfully employed in the field of petroleum.

Analysis of Petroleum Constituents.

At present, therefore, the isolation of the individual hydrocarbon components of petroleum in pure form presents unusual difficulties, and it has been possible to solve these only in individual cases. Their solution has so far been limited mainly to the low-molecular members (up to some 10 carbon atoms), and since the pioneer work of Mabery on this subject nothing strikingly new has appeared. It is clear that the same difficulties were bound to crop up again in answering the question regarding the structure of the individual hydrocarbons; some increase of knowledge in the low-molecular region is balanced out by the almost complete lack of knowledge in the region of the high-molecular members. We still stand before a vast unexplored field and hope that future workers will succeed in penetrating its mysteries. Only a few approximate solutions have been attempted in recent times in this craving for more clarity in questions of composition and constitution, and these have been from quite different points of view:

(1) Waterman has shown very neatly how the proportion of aromatic, alicyclic (naphthenic) and paraffinic hydrocarbon components of a given

sample of petroleum may be determined. He solves this analytical problem by determining first the number of aromatic rings by catalytic hydrogenation, and then by determining the total number of hydrogenated rings in the resulting mixture of naphthenes and paraffins (those originally present plus those formed during hydrogenation). This latter was accomplished by analysis or by measurements of density and refractive index.

(2) From the knowledge that tertiary hydrogen atoms in the group $\equiv CH$ reacted more easily with antimony pentachloride than secondary or primary hydrogen atoms in the groups $=CH_2$ and $-CH_3$, Schaarschmidt attempted to disclose the presence of these groups in samples of petroleum. The reaction does not appear, however, to proceed with sufficient certainty for it to give much insight into questions of constitution, and the same is true at the moment also of experiments which I have begun, and which are founded upon the steeply graded reactivity of the groups $\equiv CH$, $=CH_2$ and $-CH_3$ towards chloromethylphthalimide

$$ClCH_2N\begin{matrix}CO\\CO\end{matrix}C_6H_4.$$

(3) From an entirely different direction I myself tackled the problem of finding the constitution of the hydrocarbon constituents of petroleum more than ten years ago. The naphthenic acids already mentioned, which accompany the hydrocarbons, are, as stated above, comparatively very stable. They survive the distillation of the petroleum for the most part without change, as I found earlier with Rumanian petroleum and recently with Peruvian petroleum, and since they in all probability represent degradation products of the petroleum hydrocarbons, an acid $R{\cdot}CO_2H$ representing, for instance, a fragment formed by oxidation of a larger hydrocarbon molecule R′, an elucidation of the constitution of $R{\cdot}CO_2H$ gives an insight into at least a part of the larger molecule R′ originally present in the petroleum. This elucidation is easier with acids than with hydrocarbons, and therefore investigation of the naphthenic acids, apart from the interest shown by the acids themselves, contributes towards the knowledge of the structure of the hydrocarbon material in the petroleum.

Naphthenic Acid Constituents.

The methods adopted for the degradation of the naphthenic acids and the elucidation of their constitution were various. The most important process consisted in the conversion of a mixture of isomeric acids R_ICO_2H, $R_{II}CO_2H$, and $R_{III}CO_2H$, etc., into a mixture of the amines R_INH_2, $R_{II}NH_2$, and $R_{III}NH_2$, conversion of these by way of the quaternary methyl ammonium hydroxides into the olefines $R_I\overline{=}$, $R_{II}\overline{=}$, and $R_{III}\overline{=}$, these then being oxidized with cleavage of the group $=CH_2$ into a mixture of isomeric aldehydes and ketones. This permitted separation by means of aldehyde and ketone reagents into individual compounds, or at least allowed some of the individual compounds to be worked up, the constitution of these then being investigated. From the structure of the aldehyde or ketone thus determined, the structure of the corresponding acid could then be deduced.

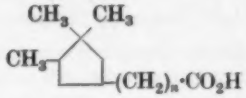
The most important results obtained in the field of the naphthenic acids are as follows:

(1) In petroleums of the most varied origin the same naphthenic acids are found; from what has been given above, therefore, the same higher hydrocarbons must be present.

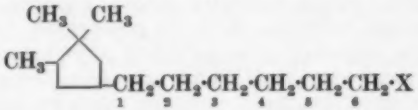
(2) The naphthenic acids correspond to two types, monocyclic, of the composition $C_nH_{2n-2}O_2$, and bicyclic, of the composition $C_nH_{n-4}O_2$.

From recent results it would appear that the latter do not consist of bicyclic rings of the type of indan or decalin, but of two separate rings.

(3) Homologous compounds are frequently met with. Thus it can be proved that the complete series of acids of the formula



(where $n = 1$ to at least 5) exists in petroleum. This is probably to be interpreted as meaning that all these acids arise from one hydrocarbon



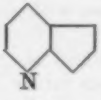
which has undergone degradation at a point somewhere between the carbon atoms 1 and 6.

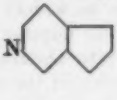
It would appear from these results that the nature of petroleum may not be so complicated as is generally assumed, and that the number of its constituents may actually fall within more modest limits.

It is characteristic of the naphthenic acids, which, thanks to the reactivity of their carboxyl group, lead to new kinds of alcohols, esters, aldehydes, etc., that the maximum molecular weight of those so far determined lies around 320 (corresponding to 20–21 carbon atoms). This has a very definite reason: on extracting petroleum with alkali, the higher members of the series of naphthenic acids form salts which are sparingly soluble in water, and these remain dissolved in the oil, from which it has so far been impossible to extract them. By means of special experimental conditions which, however, still need to be more precisely worked out, it will probably become possible to obtain these higher members and considerably extend the field of naphthenic acids accessible to the chemist. This may be of particular importance in connection with German petroleum, which is very poor in the lower naphthenic acids.

The inconvenient method of separating the naphthenic acids from each other by way of the amines and olefines has had to be adopted on account of the fact that the acid properties of the series do not change sufficiently rapidly from member to member. These circumstances are rather more favourable, however, with a further class of compounds which arise from petroleum, the nitrogen-containing bases, although it must be admitted that these are formed in some still obscure manner from primary constituents of the petroleum during distillation, and therefore present at the

moment no great interest in actual petroleum chemistry. They consist of a mixture of pyridine and quinoline derivatives, as has been shown within the last few years by careful and laborious investigations by J. R. Bailey; they also contain derivatives of the bicyclic ring systems





and are represented by numerous homologues and isomers, so that they are likely to fill many gaps in general chemistry.

Sulphur-Containing Compounds.

With regard to the sulphur-containing compounds, the form in which they exist in undistilled petroleum is still completely obscure. One thing alone is certain: they are very unstable on heating, and change very considerably and in most varied ways on distillation. In petroleum distillates we come across more or less volatile sulphur compounds which correspond to the most varied types; together with elemental sulphur and hydrogen sulphide, there are mercaptans, thioethers, disulphides, thiophenes, saturated cyclic sulphides (thiophanes), etc. It may be that some of these compounds do not arise from decomposition of the starting material alone, but from exchange reactions between primarily formed sulphur or hydrogen sulphide and hydrocarbons. It is known that not only olefines but also naphthenes and paraffins can react with sulphur and hydrogen sulphide at high temperatures, whereby a multitude of reaction products is formed. The study of these complicated relations is far from complete. Of practical importance is the question of the removal of sulphur compounds from petroleum distillates on account of their undesirable corrosive effect on metals.

II. Reactions.

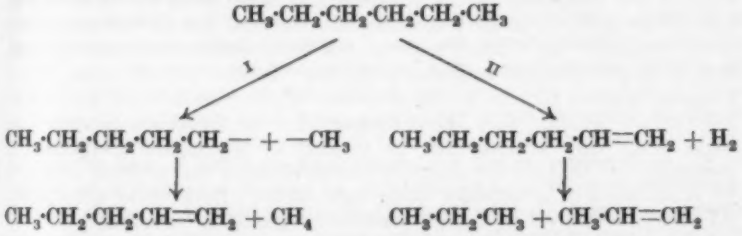
All the reactions which we can normally undertake with aromatic, naphthenic or paraffinic hydrocarbons can also be accomplished with the hydrocarbon part of petroleum. If we start with the transformation which is observed on heating petroleum by itself, without the additional effect of any chemical factors, then it can be said in a general way that the transformation consists in an increase in low-molecular material at the expense of the larger molecules, and in the formation of olefines not previously present, corresponding to the reaction

$$—CH_2—CH_2—CH_2— \longrightarrow —CH{=}CH_2 + CH_2—.$$

This formation of olefines on distilling a sample of petroleum is noticeable, although not very extensive. It might easily have suggested itself, therefore, that the extent of the change must increase if the heating process is continued, but this conclusion (like so many other apparently obvious conclusions in scientific and technical questions) was not reached. It was actually discovered, quite by accident, when the flame was occasionally left burning under a closed vessel containing oil, and since then

this method of treating petroleum, which changes its original character very considerably, has become one of the most important operations in the petroleum industry. This has been the case for decades, the treatment being designated in all its variations and ramifications as a cracking process. It is so widely known that I can dispense with descriptions of the details. The number of the processes, which often differ only in minor details, runs into thousands. In general the material is cracked either in the gaseous or in the liquid phase. In both cases larger molecules are broken down to smaller saturated and unsaturated molecules, and in both cases the unsaturated molecules reunite to form larger ones: they polymerize. This polymerization is more extensive in liquid-phase cracking than in gaseous-phase cracking. In addition to these two fundamental primary alterations of the petroleum material there are a few further secondary changes (isomerization, etc.). The whole transformation process is promoted by the presence of such substances as aluminium chloride.

Petroleum cracking operations, which may be regarded as a deliberately intense, prolonged distillation of the petroleum, have been investigated in a purely empirical manner in the laboratory for a great many years. It has not yet been possible, however, to determine the laws which control cracking, in spite of the fact that such men as M. Berthelot and F. Haber, then Wheeler, Thorpe, Young and many other prominent chemists, have taken part in the experimental treatment of the question. It is only recently that any light has begun to be thrown on the matter, arising partly from thermodynamic considerations and partly from ideas of bond strengths based upon electronic theories. The example of *n*-hexane may be taken by way of explanation:



If we consider what can happen at high temperatures to such a hydrocarbon as hexane, we find that a weakening of either the C—C bond or of the C—H bond could take place equally well. It can be shown thermodynamically (*a*) that the reaction I is more probable than reaction II, and (*b*) that the ends of the molecules are thereby preferentially attacked, excepting with high molecular paraffins. In case I (see the structural formula above), the readjustment—after the first phase is over—leads to amylene and methane (hence the abundant appearance of the latter during cracking); in case II the hydrogen split off attacks the molecule at the bond in β-γ position to the double bond, on account of the intrinsic weakness of such linkages, and propane and propylene are formed. The results of experimental research agree with this, just as they agree with a whole series of further theoretical demands such as the following:

(1) Reaction according to II will favour larger molecules rather than smaller molecules.

(2) The decomposition of an olefine (*e.g.*, $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH = CH_2$) into acetylene and a paraffin, in contrast to earlier assumptions, is quite improbable.

(3) The polymerization of olefines is favoured at lower temperatures rather than at higher temperatures.

(4) Conversely, the higher the temperature the more the dehydrogenation of naphthenes to aromatics is favoured.

(5) A dehydrogenation of aromatics (benzene $\longrightarrow$ diphenyl), which gradually leads to coking, can well be expected from thermodynamic considerations, but not a similar fusion of paraffin molecules. And so on.

In a few words it may be stated that the behaviour of aromatic hydrocarbons is characterized by weakness of the C—H linkage, whilst that of aliphatic hydrocarbons is characterized rather by weakness of the C—C linkage.

It is exceptionally interesting that the views on the origin of petroleum in Nature which have long been the subject of speculation are also affected by these observations. Of the two theories on the origin of petroleum, the inorganic (from metallic carbides) and the organic (from vegetable and animal matter), the former had to be abandoned when it was found that petroleum was optically active and contained traces of sterines, hormones and porphyrines. The question remained open, however, in what circumstances and conditions the transformation of flora and fauna into petroleum could have taken place. Here the previously mentioned thermodynamic considerations came to our assistance. They showed, since at low temperatures the paraffins and naphthenes are more stable than the aromatics, that the transformation of organic matter into petroleum must necessarily have taken place at low temperatures and have yielded first of all paraffins and naphthenes (in the paleozoic period), after which a transformation process in the direction of the paraffins set in (in the late tertiary period); they show, further, that the formation of aromatics could occur only at intervals, on account of the higher temperatures necessary, and that the formation of petroleum from coal which is assumed by some workers is actually quite improbable. Here again theoretical chemistry has helped us to find solutions for geological problems.

It is well known that one of the most important technical achievements of recent years in the field of chemistry is catalytic hydrogenation, which enables us to attack and find solutions for problems which were hitherto insoluble. I have mentioned it already quite briefly in connection with Waterman's experiments. It is of even more importance for preparative work in the field of petroleum. If we allow hydrogen to react on a cracked oil containing constituents such as olefines and aromatics which are susceptible to hydrogen, or if we combine cracking and hydrogenation into one operation—we speak then of destructive hydrogenation—we obtain an oil which now belongs to the paraffin class and which is much richer in valuable petrol than was the starting material. Many details of these relations are probably well known also, and I shall not need to go into them further here. I shall only indicate that petroleum hydrogenation reactions as well as cracking reactions are now being examined from a

thermodynamic standpoint, and for many points that were already known a clear explanation has been found. I should like to emphasize here the following: hydrogenation, and the opposed reaction, dehydrogenation, are as a rule at equilibrium with each other; it depends on temperature and hydrogen pressure which of the two reactions comes into play. The considerations here are naturally very similar to those given for cracking. It is worth mentioning that by removing olefines as they are formed, polymerization is repressed. On account of the tendency of aromatics to coke, it is necessary to work at as low temperatures as possible, and in consequence also with as good catalysts as possible. The side-chains of aliphatic-aromatic hydrocarbons are easily broken off by the entry of hydrogen. The hydrogenation of naphthenes to paraffins is possible, as was mentioned in speaking of the geological relations of petroleum.

The unsaturated compounds formed on cracking petroleum are among those which most interest the chemist, on account of their particularly high reactivity. This reactivity is due to additions on the double linkage. Reactions between the unsaturated compounds and outside substances will be dealt with later; the unsaturated compounds can, however, combine with each other, when the transformation known as polymerization takes place, the simplest example being:

$$CH_2{=}CH_2 + CH_2{=}CH_2 \longrightarrow CH_2{=}CH{\cdot}CH_2{\cdot}CH_3.$$

I have mentioned that during cracking a partial undesired polymerization occurs. The idea suggests itself that this may be made more intensive where it is desired to build up large molecules from smaller ones. This problem has been approached remarkably late—only in recent years, in fact—in the field of petroleum. With the aid of the cracking products of petroleum of low molecular weight it has been possible to solve it already so far as to increase the yield of petrol from petroleum in America by 5 to 10 per cent. The course of the formation of this so-called polymer gasoline is only partly explained: the matter is not altogether so simple as in the above example showing the formation of butylene from ethylene. We are concerned with a problem which increases in interest from day to day in other fields of chemistry too, and is becoming of the greatest importance in the manufacture of resins from compounds such as styrene, acrylic ester, *cyclo*pentadiene, etc. It is to be anticipated that the steady advance in the understanding of polymerization processes will also throw considerable light on the formation of polymer gasoline.

Polymerization is assisted by physical factors such as the silent electric discharge, and also, like cracking, by the presence of many substances, amongst which boron fluoride, and especially aluminium chloride, may be named.

Reactions which take place in the presence of aluminium chloride are amongst the most prolific in organic chemistry. Even Friedel and Crafts, who introduced the reagent, realized that with its help it was not only possible to bring about the removal of hydrogen halide between an aromatic hydrocarbon and a non-aromatic halogen compound, but that hydrocarbons by themselves were also liable to considerable alteration in its presence. This occurs with petroleum as well, and it has been, amongst other things,

consideration of this material which has led a number of chemists to examine these reactions more closely during the last few years. A very interesting conclusion has thereby been reached: we know now that the rôle of the aluminium chloride—probably on account of the transient formation of complexes—consists fundamentally in an ability to weaken C—C and C—H linkages and so promote, for instance, dehydrogenation, cracking and isomerization, which are achievable by the action of heat alone. Aluminium chloride is further capable of initiating the combination of paraffins with olefines, a reaction which was previously known only for aromatic compounds, and it presents thus a striking example of a substance from which much that is new may yet be expected, particularly in the field of petroleum.

The olefines in petroleum behave like the olefines of other origin, both in their ability to combine with each other and in their ability to combine additively with other substances: with water to form alcohols, with hydrochloric acid to form monochlorides, with chlorine to form dichlorides, with organic acids to form esters. These reactions do not present anything new chemically, but they are noteworthy on account of the range in which they can be carried out with the material at our disposal. This will be treated briefly in the next section.

The substitution reactions which can be carried out with the petroleum paraffins, chlorination, nitration with dilute nitric acid, and sulphonation, are exactly the same as those which can be carried out with paraffins of other origin, and present nothing fundamentally new. The sulphonation reaction is probably the most interesting, since it occurs to a certain extent during the purification of the crude oil by scrubbing with sulphuric acid, and still presents points which are difficult to understand. This should act as a stimulant to a closer investigation of the sulphonation of paraffins and naphthenes than has been the case in the past with hydrocarbons of known constitution.

It is readily understandable that petroleum, like almost all organic substances, is susceptible to the action of oxygen; the formation of gums in petrol and to a great extent the diminution in the valuable properties of the higher molecular fractions of petroleum—notable for their lubricating properties—are due to this phenomenon which is known as ageing. In the case of petroleum, as in other cases, some reduction in this can be brought about by using the inhibitors of oxidation (phenols and their derivatives) which Moureu and Dufraisse found during the war for stabilizing the very unstable acrolein, and which are effective even in very small quantities. Until a short time ago, deliberate oxidation with a definite object (which could naturally be accomplished in many directions) had, in contrast to this undesired, injurious and disturbing oxidation of the petroleum, yielded no scientifically or technically noteworthy results. Only recently have any of these been obtained in the technical field to be described in the next section.

III. Technical Progress.

So far we have said little about the technical advances which have been made. Such advances and their relation to the scientific achieve-

ments in the field of petroleum during the past sixty to eighty years will now be briefly mentioned. They will be considered in connection with the individual petroleum fractions as follows, these being arranged in order of increasing boiling point and molecular weight:

(1) Lowest boiling fractions.
(2) Gasoline.
(3) Kerosine.
(4) Gas oil, spindle oil, etc.
(5) Paraffin wax.
(6) Asphalt.

About the middle of the nineteenth century kerosine was probably the only petroleum product of any importance. This importance has perhaps decreased somewhat with the introduction of other means of illumination, although the quality of the oil has been considerably improved by the application of Edeleanu's process, which removes the smoke-producing constituents with sulphur dioxide.

In connection with fraction (1), all the developments which have arisen are entirely new—*e.g.*, the transformation of low-molecular olefines and paraffins into alcohols, chlorides, glycols, etc., which have thus become available in unlimited quantities, and can sometimes be prepared more easily from petroleum than by other methods. The possibility exists, of course, of working up the higher hydrocarbons in a similar manner if a demand for such products should arise, and especially if some easier way of isolating individual components were found. Methane can also be included in fraction (1) and it is well known how enormously varied its technical applications have become in recent times. Their enumeration would far exceed the limits of this lecture, and it is probably sufficient if I mention only the possibility of preparing acetylene by dehydrogenation of methane. Concerning the higher hydrocarbons, the pentanes may be converted by way of their monochlorides into amyl alcohol, and acetone may be synthesized from propylene according to the equation

$$CH_3{\cdot}CH{=}CH_2 \longrightarrow CH_3{\cdot}CH(OH){\cdot}CH_3 \longrightarrow CH_3{\cdot}CO{\cdot}CH_3.$$

An entirely new development is the reaction of propylene with chlorine at high temperatures, which leads surprisingly enough to glycerol:

$$CH_3{\cdot}CH{=}CH_2 \longrightarrow CH_2Cl{\cdot}CH{=}CH_2 \longrightarrow CH_2Cl{\cdot}CHCl{\cdot}CH_2Cl \longrightarrow CH_2OH{\cdot}CHOH{\cdot}CH_2OH$$

The gasoline fraction of petroleum is a mixture of compounds which has acquired a hitherto-undreamed-of significance, and has been the subject of exceedingly important advances concerning both its quantity and its quality. The increase in its quantity has been brought about on the one hand by perfection of the cracking process, and on the other hand by introduction of polymer gasoline. An improvement in the quality has been achieved by an extended study of the phenomenon of knocking and of methods for its elimination (removal of paraffins of medium molecular weight or addition of olefines of medium molecular weight). The implications of this phenomenon are still not clearly understood.

Neglecting for the moment fractions (4) and (5), and considering asphalt, the residue from the distillation of petroleum, we find a product which is technically of very great importance, but which has been the subject of very little chemical investigation. It is likely to be a particularly fruitful task for the future, to attack this problem with the utmost resources of modern chemistry.

The solid hydrocarbons of the paraffin-wax fraction (5) remained undeveloped until recently. Now, however, it has been found that they can be oxidized on a technical scale and can be degraded, yielding products similar to those obtained from fats (palmitic and stearic acids), which serve for the manufacture of soap.

The components of fraction (4) are of quite particular interest, not only because they yield the fuel for diesel engines, but also because this fraction contains most of the compounds which possess valuable lubricating properties. The deficiency of these compounds in German petroleum has led to recent attempts to manufacture them artificially. For this, however, a knowledge of the structural requirements which are associated with good viscosity and good lubricating power is wanted. With that reference I may conclude this enumeration of technically important problems in the field of petroleum, some of which have been completely, and some of which have been only partly solved.

CONTRIBUTION TO THE STUDY OF THE CHANGES OCCURRING IN LUBRICATING OILS IN INTERNAL COMBUSTION ENGINES.*

By Prof. H. Weiss and Dr. A. Maillard.

In the working of the internal-combustion engine, the lubricating oil serves the double purpose of lubrication and of heat removal. When, for any reason, these effects are not produced, the result is certain to be serious damage to the engine, and sometimes, as in the case of aero-engines, actual disaster.

One of the causes of such damage, and perhaps the most frequent, is excessive change in the condition of the oil; deposits may be formed, the effect of which is to choke up the oil feeds, and thus, by preventing lubrication, cause a breakdown: or rapid ring-sticking may take place, an occurrence which will soon put the engine out of working order.

This shows how important it is to know the nature of the changes taking place, and the interest which the user has in preventing too great a change in order that he may not have to suffer from its effects.

To avoid such accidents, it would be best, of course, to use a lubricant which does not alter in use. Unfortunately, such lubricants do not yet exist. The choice must therefore be made from amongst those which show least tendency to alter.

How can this choice be made? It is obvious that some artificial form of ageing must be applied, such as an oxidation, and that its effects must be measured. This, indeed, is the object of all experimental work on artificial ageing.

Several methods are in use; they all include at least three factors: temperature, contact with oxygen pure or diluted, and time. Some, in addition, involve the use of a catalyst.

They differ from each other only in the method of effecting the change, or by the way in which the change is measured. Such procedure is too well known to be dealt with here; it is sufficient to recall that the problem of the alteration of motor oils in use has been the subject, in almost all countries, of many outstanding investigations to which we have made a point of paying close attention at the time of their publication.

We ourselves have been studying this question for several years (since 1933 for motor oils). Our present paper is derived from the results of many and varied experiments, and should be regarded as our contribution to the general study of the subject as applied to internal combustion engines.

Our studies include experiments *in vivo* on various engines in service; observations on experimental engines have enabled us to elucidate particular points regarding oil change, as we had not then to take the fuel into account.

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* Paper presented for Discussion at the One Hundred and Eighty-second General Meeting of the Institute of Petroleum held on May 10th, 1938.

Lastly, we have undertaken a study of oxidation in the laboratory. In this study we have adopted a method of treatment, the conditions of which have been suggested by our observations on motor engines in use.

Regarding the " measure " of the change effected in each particular case, we must own that we have not yet discovered a variable or group of variables the determination of which will give a faithful and complete picture of the future behaviour of an oil in the engine.

The procedure which we shall describe later on in the paper must not be considered as just one more method of test, but as a means towards the clarification of at least one aspect of the complicated whole which composes the process of oil change.

The study of oil change *in vivo* has been made both with diesel and spark-ignition engines. It has taken into consideration variations of the following characteristics: density, viscosity, acidity, saponification number.

It has also included the determination of the ash content and of the products precipitable by light naphtha. We attach a particular importance to that portion of these products which is insoluble in chloroform. Such material is also insoluble in hot oil, and thus may be particularly dangerous.

Without entering into all the details, the principal results of our observations are as follow:

Diesel Engines.

Marine Engines.

We have taken, or have had taken, samples from the crank-cases of both principal and auxiliary engines. The results of these experiments, a part of which has already been published,[1] may be summarised as follows, though we shall take only one case as regards the actual figures:

The increase of density, viscosity, acidity, ash content, and of the quantity of oxidation products precipitable by light naphtha is very regular, and is in proportion to the length of service.

Thus, for example:

Density at 20° C., which was 0·914 for fresh oil, increased to 0·934 after 1200 hrs. in use.

Viscosity, in the same conditions, increased at 20° C., from 6·87 poises to 17·83 poises; at 50° C., from 0·835 poises to 1·515 poises.

Acid Value from 0·01 (mg. KOH/gr. oil) to 0·68.

Ash from 4·6 (mg./100 cm.^{3} oil) to 127 mg.

We may mention, in passing, that in one case under observation determination of the ash and its analysis shows an influx of sea-water from a leak in the oil cooler, and gave the approximate time when the damage occurred (150th hour). In addition, it showed that the repair (at the 500th hour) has not been effective.

As regards the precipitable products, we have determined the fraction that is insoluble in chloroform, this being approximately the same as that which is insoluble in oil. Table I relates to a 1200 hrs.' experiment. It appears from these figures that the fraction insoluble in chloroform is the most important (72 per cent. on the average), and that the fraction soluble in cold oil, and which can be precipitated by naphtha, is less than 10 per

cent. The sixth column of the chart shows that after precipitation there remains a quantity of oxidation products as great as before, which proves that this manner of measuring oxidation still leaves something to be desired.

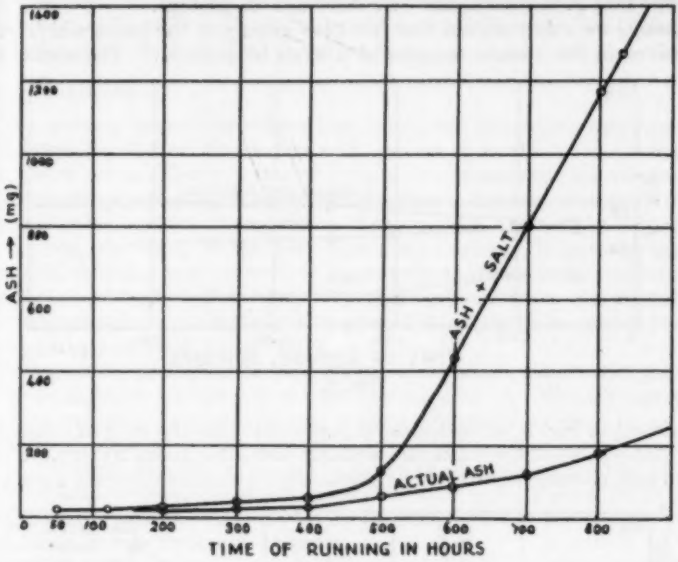

FIG. 1.

The percentage composition of the total deposit is shown in the following chart, which shows that the constituent the amount of which increases is really the part insoluble in chloroform.

Investigation of the sulphuric acid tars and the variation of the critical

TABLE I.

Results of Precipitation Tests on 100 cm.³ of Oil.

Time of Running, hours. (1)	Total Deposit in Unfiltered Oil. (2)	Part Soluble in Chloroform. (3)	Soluble, %. (4)	Deposit Precipitated from the Filtered Oil. (5)	Deposit Precipitated from the Filtered Oil in the Presence of NH_3. (6)	Ratio, col. (6)/ col. (5). (7)
0	0	0	0	0	0	0
10	66	17	26	3·1	11	3·6
20	85	18	21	4·6	12	2·6
50	107	27	25	7·7	15	1·9
100	134	46	34	10·8	23	2·1
200	175	55	32	13·8	39	2·8
400	216	82	31	16·9	62	3·7
800	569	121	21	37·8	82	2·2
1200	861	278	32	67·7	130	2·2

temperature of solution in a mixture of acetone and amyl alcohol clearly show the regular increase of the oxidation products. At the same time, distillation in cathodic vacuum of fresh oil and oil in use for 1200 hrs. showed that in this particular case there was no dilution.

Lastly, we may mention that we have extracted the gases which were dissolved in the various samples of a series of extracts.[2] The results are

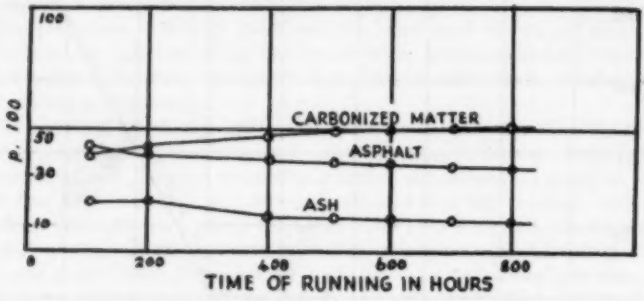

FIG. 2.

expressed in Fig. 3, which shows, in particular, that the oxygen content of the atmosphere of the crankcase is nearly zero after about 200 hrs., so that from that moment there could be practically no more oxidation in the crank-

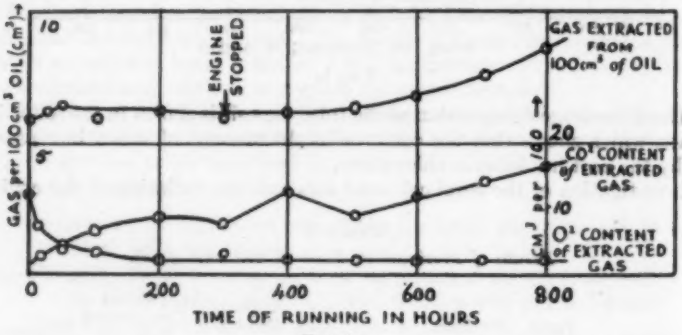

FIG. 3.

case. It is taken for granted, of course, that the dissolved gases are in equilibrium with the atmosphere.

All the foregoing experiments were made with engines unequipped with filtering systems and in the oil of which oxidation products accumulate.

This was not the case, however, with observations made on principal engines (6000 h.p., 120 r.p.m.), equipped with an oil-filtering system which could be started up as occasion demanded.

The analysis of oil samples drawn from such engines shows no regular variation in the characteristics. This was to be expected, for simple filtration, as shown by the figures of a preceding chart, can retain more than 80 per cent. of what we have called total deposit. The only certain in-

formation which we have gathered from these last experiments is this: in such engines the crank-case is separated from the cylinder, and consequently no "unburnt residue" or soot can pass from one to the other. Nevertheless, the deposit formed in the oil is insoluble in chloroform in the proportion of from 70 to 75 per cent., which clearly indicates that these are oxidation products from the lubricating oil.

Diesel Locomotives.

Two series of experiments have been made, the first with engines on the test bench for 72 hrs., the second with engines in service. On the bench, the oils of seven different types of engines were examined, the determinations previously indicated being made. Since, however, the trials were made in order to study the operation of the engines, and not the behaviour of the oils, the observations were somewhat limited. It is to be noted, however, that they entirely confirm those made on the marine diesel engines. The figures arrived at show a regularly progressive increase of the products of change in the oil, particularly those precipitable by naphtha, and including both soluble and insoluble in $CHCl^3$.

The quantity of deposit formed during a particular time varies greatly from one engine to another—in as wide a ratio as 1 to 15. We only regretted we were unable to lubricate several engines with the same oil. If, on the other hand, we consider the amount of "insoluble in chloroform" existing in the different deposits extracted from crank-case oils at the end of the experiments, we find that it varies only between quite narrow limits and that it always remains high—about 85 per cent.—results which agree with those arrived at with marine engines.

The acidity and the saponification number also increase regularly. In the case of the ash content the variation is quite irregular. Sometimes it increases, sometimes it decreases. We have explained the decrease by regarding the engines in question as being in the running-in period, and that metallic particles which circulate at the beginning of the experiment are deposited during the periods of rest, remain out of circulation, and consequently are not drawn out when the sample is taken.

In service, the results are more irregular, although they still agree with the previous observations, particularly as regards the formation and composition of the deposits, 70–80 per cent. being insoluble in chloroform.

Automobile Engines.

In automobile engines the same factors of oil change exist. On the other hand, if the number of hours of service of motor oils is much less than that required of oils for diesel engines, or at any rate for marine diesel engines, the service required of the former is intermittent. It is practically impossible to determine this effect, particularly on engines in normal service. We tried, however, to estimate its importance by means of special experiments made with the following engines:

A Renault KZ5 11-h.p., a Citroen 14-h.p., a Renault 8-cyl. 24-h.p., for the study of the formation of oxidation products. A Peugeot 6-h.p.-4 cyl. to study the effect of intermittence of service.

Experiments with 11-*h.p. Renault Engine.*

At the time of the first experiment this engine was lubricated with a medium heavy oil and ran 7000 km. without changing the oil. The following figures relate to the oxidation products:

Number of km.	Total Deposit, mg./100 cm.³.	Insoluble in $CHCl_3$, %.	Deposit in Filtered Oil, mg./100 cm.³.	Acidity, mg. KOH/100 cm.³ Oil.
611	108	31	6	9·35
1643	167	35	8	12·9
2834	280	38	11	15·8
4908	411	44	14	20·9
7045	611	60	24	49·6

This oil practically maintained its original viscosity.

The ash was composed of iron oxide to the extent of 95 per cent.; the total amount of iron oxide corresponded to a wear of the cylinders of 2 microns, considered as uniform.

We must point out that in this particular case the oil retained iron soaps in solution which we were able to separate by washing the oil with water, and evaporating the aqueous solution. Likewise, ashing of the sulphuric acid sludges obtained from the filtered oil left a slight residue of Fe_2O_3, whereas the acid used in the experiment contained no trace of iron.

The coefficient of friction of the oil remained practically constant. The values obtained with the Herschell apparatus were:

Km.	Coefficient.
0	0·82
611	0·70
1643	0·95
2834	0·82
4908	0·84

An experiment with a solvent refined oil has given similar results with, however, a smaller proportion of material insoluble in chloroform (20 per cent. on an average). In both cases the dilution was not above 3 per cent.

As regards the Renault 24-h.p. and Citroen 14-h.p. engines, the results observed are similar, with the exception that there was an accumulation of mineral matter in the deposit. This mineral matter was introduced with the fuel, and had nothing to do with the lubrication. We should like to point out, however, that such a condition can ruin an engine in a very short time.

The "Peugeot 201" 6-h.p. engine was used to study the influence of interrupted service on automobile engines.

We have shown above that in the case of the diesel engine the oxygen content of the crank-case atmosphere decreased. The same phenomenon should happen with the motor-car engine if the latter worked continuously and with a closed crank-case; but as it works intermittently, equilibrium composition of the atmosphere can re-establish itself when it is not working.

On the other hand, as the engines are not perfectly air-tight, some gases

always escape from the combustion chamber into the crank-case. These have low oxygen content, so that the oxygen content of the crank-case atmosphere must decrease.

The experiment was made in the following way: the oil breather of the engine being closed, gas was extracted through a tube specially fitted to the crank-case at time zero (just before starting); then at intervals of 3 mins., when the car was running at a speed of about 50 km. per hour.

The results were as follows:

Time (mins.):	0.	3.	9.	12.	15.	18.	21.	24.	27.	30.
O_2 % .	20	18·4	16·7	16·5	15·6	15·1	14·6	14·2	13·6	13·2
CO_2 % .	0·5	0·8	1·7	1·7	2·2	2·2	2·1	1·8	1·8	1·6

A second experiment, with oil breather open, made during a run of 1½ hrs., with fortuitous stops, showed that during the stops the oxygen content went up again; in the conditions of this experiment, which are those of normal use the oxygen content remained at about 13 per cent.

It is very likely that with a more air-tight engine we should arrive far more quickly at an atmosphere containing practically no oxygen.

We may say, then, that in normal good conditions the atmosphere of the crank-case has lost about half of its oxidation power. Moreover, the oxidation of the oils at the temperature of the crank-case always leads to the formation of products completely soluble in chloroform, whereas the engine produces products partly insoluble. It seems difficult, therefore, to admit that these troublesome oxidation products are formed in the crank-case. It seems more likely that the cylinder and the piston are the principal seats of the change, in view of their much higher temperature (200–400° C., according to Legrand).

(The following fact seems to confirm this conclusion. A piston was taken from an engine after 60,000 km. run without overhaul. The piston was black half-way up. The deposit was removed in bands parallel to the piston head and examined. The bottom band was completely soluble in chloroform. That at the top was practically insoluble. If this insoluble substance had been soot, it would also have been found in the lower bands. It is obvious that we have here zones of temperature decreasing from the top.)

On the whole, all our observations on automobile engines in service agree as regards precipitable oxidation products. Considering the nature of these products, we are led to believe that the hottest parts of the motor are those where the oil is most affected, the temperature being a preponderating factor in oxidation. This temperature factor has the peculiarity that it cannot be varied indefinitely. There is a temperature at which cracking of the oil occurs. It may be wondered whether such cracking may be considered as part of the complex series of reactions which we refer to as deterioration. In order to ascertain the fact, we have made tests of the resistance to heat of a certain number of lubricating oils, by heating them under atmospheric pressure until permanent gases were formed.[3] The values found for the pure mineral oils experimented with were all above

380° C. Castor oil, on the other hand, decomposes at about 250° C. with formation of water and products which distil at that temperature. Olive oil decomposes at about 310° C.

Even if it does not seem, at least with pure mineral oils, that straight pyrolysis can play an important part in motor oils, it is quite possible that this phenomenon will soon have to be taken into account in the lubrication of air-cooled aero-engines, where the temperature of the cylinder heads rises very high.

Another point which attracted our attention was the possibility of influence of the gaseous or liquid products from incomplete combustion on the process of oil change. This led us to try to separate these products, which are acid and unsaturated. They make up a large part of what is called the "diluent," which is composed not so much of fuel escaping during compression as of partly burnt and cracked fuel which has escaped into the crank-case during combustion owing to the high pressure existing at that moment.

We made the following tests with a view to the identification of these products in order, if necessary, to study their influence upon the oil.

The exhaust of a 5-h.p. Peugeot engine was fitted with a coil-type cooler to allow condensation of water of combustion and part of the products of incomplete combustion. The liquid fraction of the latter was distilled and its iodine value determined. At the same time the diluent from the crank-case oil was subjected to the same treatment. The close relationship of the two products is apparent:

	Product from Exhaust Pipe.	Product from Crank-case Oil.
Distillation range	130–280° C.	140–285° C.
Unsaturated and aromatic products . .	20–35	20–30

(The fuel itself distilled between 80 and 220° C., the oil did not distil under 350° C.)

The results concerning non-saturation agree closely with the work of Levi [4] and Orel.[5]

Lastly, we have been able to show,[6] in addition to unsaturated products and acids (formic and acetic acids, for example), the simultaneous presence of phenols and aldehydes (among them C_6H_5OH and HCHO).

This fact is of importance, for it permits an explanation of formation of resins in the engine itself, and this may play a certain part in ring-sticking.

All the same, the tests *in vivo*, the tests on experimental engines of which we are now going to speak, and the artificial ageing tests, which we reserve for the end, all combine to show that the action of the products of incomplete combustion is not of major importance in the formation of the products insoluble in lubricating oils.

The following is typical of experiments undertaken in this direction.

A single-cylinder petrol engine (Peugeot) was run for a fixed time, with measured quantities, successively, of hydrogen, coal gas and motor-spirit as fuel. Up to the present we have not been able to make a great number of such tests. Our results, however, although still lacking in precision, make

it certain that the unburnt fuel can play but a very small part in the formation of sludge. Here are only a few figures : [7]

	Sludge Formed in the Oil during 10 Hrs.' Run (mgm./100 gr. Oil).	
	Total Amount of Sludge.	Insoluble in $CHCl_3$, %.
Run with hydrogen . . .	105	48
,, coal gas	90	68
	89	73
,, motor-spirit . . .	126	50
	151	45

The accuracy of these figures is about 10 per cent., because of the small quantity of oil in circulation. They show clearly, however, that the great part of the sludge has its origin in the oxidation of oil, and not in the incompletely burnt fuel, whether the sludges are liquid or solid residues (soot).

Further experiments [8] were carried out on the oxidation of the oil on the piston. The object was the study of the formation of hard carbon. For this purpose the engine previously referred to was run on hydrogen. The formation of hard carbon was followed by weighing the piston after washing it free of oil. The results of the test were as follows :

The oil, as the only hydrocarbon present in the engine, was enough to produce hard carbon ; but this hard carbon was very hard, brown and of the appearance of varnish. It does not resemble the hard carbon found in the combustion chamber of motor-engines run with petrol. Two tests, one with fresh oil, the other with an oil which had been used for 3000 km. in a touring car, have shown that in that particular case the age of the oil had no influence ; the amounts of hard carbon formed have been the same in both cases within the limits of experimental error (10–15 per cent.).

The figures for 450,000 revolutions of the engine were :

Fresh oil 118 and 103 mg. of hard carbon.

Oil already used : 109 and 130 mg. of hard carbon.

Comparative tests (same temperature of the cylinder head), running the motor with petrol instead of hydrogen, gave the following results :

(*a*) The amount of hard carbon formed on a clean piston is less than with hydrogen.

(*b*) The condition of the piston surface influences the amount of hard carbon. Hard carbon already formed acts as a retainer. The lubricating oil is absorbed by it, and is carbonized, as shown in Fig. 4. After a given running time the amount of hard carbon formed increases with the amount of hard carbon already existing on the piston.

When the engine is run with a rich mixture of fuel and air, a very small amount of hard carbon is formed ; moreover, it is very light, and is not adhesive. The conclusion reached from these tests is that incomplete combustion of the lubricating oil is chiefly responsible for the formation of hard carbon. The extent to which it remains on the piston and its adherence, however, seem to be mostly a question of carburation.

The transformation of the lubricating oil into water and carbonic acid was determined with the same engine running on hydrogen.[9] Thus we had only to determine the amount of carbonic acid in the exhaust gas (this determination has proved rather delicate).

Many tests have been made; they have all shown that oil consumption due to combustion proper is very small. In the engine which we used in

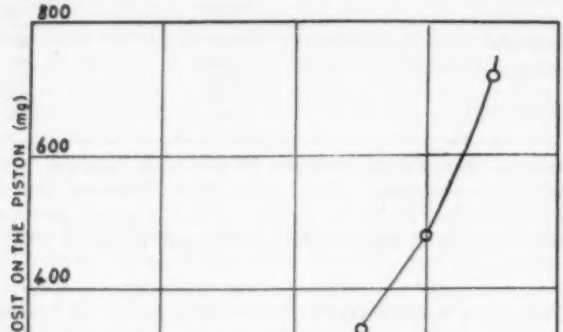

FIG. 4.

our tests (Peugoet 175 c.c.) it amounted only to 4 gm. per hour on an average, *i.e.*, one-tenth of the consumption of the engine when it is used on a motor-bicycle; the remaining nine-tenths are lost mechanically (oozing out along the plug-rods, very fine atomization followed by escape with the exhaust gas).

The principal results of all these observations on engines can be summed up in the following way :

1. Oil deterioration is chiefly caused by oxidation. The most dangerous products are sludges insoluble in hot oil. They are also insoluble in chloroform.

The origin of these sludges is actually the lubricating oil, and not the fuel; it may be accepted, however, that incomplete combustion products of the fuel may in some cases be found in the oil. From these products we have been able to isolate substances capable of forming resins (phenols and aldehydes).

2. The seat of the formation of insoluble oxidation products is the

cylinder. It does not appear that oxidation in the crank-case need be taken into consideration for the formation of these products because :

(*a*) The temperature in the crank-case is too low (80–120° C.) ;

(*b*) The atmosphere of the crank-case quickly loses a great part of its oxidizing power because of the blow-by ;

(*c*) It does not seem that pyrolysis, properly speaking, plays an important part in the alteration of the oil, at any rate not in ordinary engines. It is, of course, unquestionable that it occurs in the combustion chamber.

These conclusions, in a certain way, limit the conditions of the laboratory researches.

Laboratory Tests.

Concerning the temperature of the tests, it will be necessary to make the experiments at temperatures of the same order as those observed under the piston, in order to obtain an oxidation similar to that produced in the engine.

Concerning the other factors which are to be met with in the engine (varying pressure, contact with oxygen, etc.), it does not seem possible to reproduce these in laboratory apparatus.

We are, however, designing a special engine which will allow us to realize these conditions approximately.

Our first care has been to determine the temperature of operation. As a criterion of the similitude of the artificial oxidation products with those which are produced in the engine, we have chosen the amount of sludge insoluble in chloroform.

As we have shown, these insoluble products are always found in used motor oils. We know that some authors consider these insoluble products to be soot. We do not agree with them, and we think we have proved our opinion.

There are two more facts which may be borne in mind :

1. Artificial ageing tests at very high temperatures [10] have led to the formation of sludges insoluble in chloroform in a proportion of at least 80 per cent., and there is no soot present.

2. Extensive study of oil oxidation at lower temperatures, of the order of those existing in motor-car crank-cases [11] has never led to the formation of products insoluble in chloroform.

The experimental process which we have adopted in our laboratory researches is as follows :

The oil is oxidized by a current of air which bubbles through it under fixed conditions. The oxidation flask, of the shape shown in Fig. 5, also allows good contact of the oil with the atmosphere in the flask. The test is carried out on 50 c.c. of oil. The size of the flask is such that it can be weighed on a precision balance ; it is shaped in such a way that volatile products escape completely and that it can be easily cleaned.

The volatile products pass to a second flask, where they are condensed and weighed.

So far we have only determined the acidity, but we intend to make more complete analyses later.

The first flask is heated in an electrical resistance furnace, the temperature of which can be maintained constant; the maximum operating temperature is 400° C.

The precipitation of oxidized matter and the filtration are made in the usual way, and taking all necessary precautions.[12]

Determination of the Temperature of the Experiment.

It is quite obvious that there is no well-determined temperature above which the oxidation of the oil leads to the formation of products insoluble in chloroform. Other factors play a very important part in this oxidation.

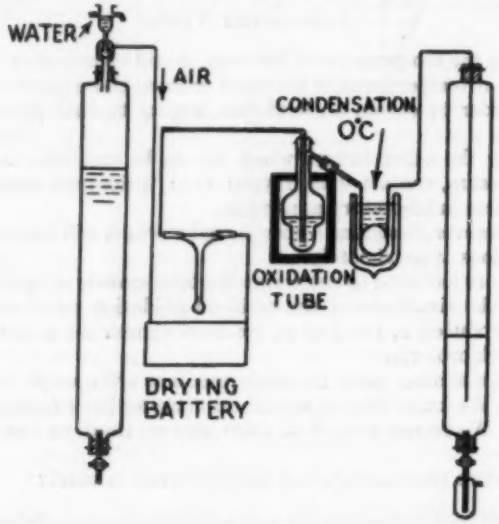

FIG. 5.

What we wished to determine was the order of magnitude of the temperature at which, after a reasonable time, there is formed a proportion of insoluble products similar to that met in the sludge of used oils in practice.

The following results, amongst others, were obtained with a medium viscosity motor oil after 8 hrs., air being circulated at 500 c.c. per hour.

Temperature. ° C.	Per 100 c.c. Oil.		
	Loss of Weight.	Sludge.	Sludge Insoluble, %.
200	0·3	0	—
250	1·3	0·071	36·6
300	2·8	0·126	39·0
350	4·7	0·198	40·8

It will be seen that, under the conditions of test, it is necessary to go to 300° C. in order to obtain an amount of sludge sufficient to be easily weighed. At this temperature the proportion of matter insoluble in chloroform is similar to that obtained in the engine.

Air Circulation.

The tests have been carried out on rates of from 200–600 c.c./hr.

Circulation, c.c.	Loss of Weight, %.	Volatile Matter, %.	Total Amount of Sludge.	Insoluble in $CHCl_3$, %.
200	0·07	0·6	0·100	50
280	0·54	0·11	0·106	56
360	0·68	1·67	0·136	50
360	0·73	1·82	0·138	51·5
480	1·21	2·56	0·161	51·5
600	1·34	3·3	0·176	48

The rate of air circulation does not seem to change the character of the sludge. The same may be said of the duration of the treatment; the amount of oxidation products increases regularly with the time; its composition does not change perceptibly, it being understood that the duration of the test does not exceed 8 hrs.

In our first tests we estimated the amount of oxygen combined with the oil from the loss of weight of the oil and the amount of volatile substances collected. In the last series of tests we determined it by direct measurement of the amount of air introduced into and coming out of the apparatus. The analysis of the remaining air was used as a check on the determination.

The amount of oxygen taken into combination is practically in direct proportion to the time, with the exception of a delay at the beginning of the reaction. Under our operating conditions the amount of oxygen combined is over 50 per cent. of that introduced into the apparatus.

The following are some results obtained on a few commercial oils. If we classify the oils by increasing density, we find that the acidity of the volatile substances is the higher the lower the density. On the other hand, precipitable substances increase with density. The compounded oils do not behave well in the test at 300° C.; vegetable oil is decomposed.

Oil.	d_{20}.	20 dynes/cm.².	Loss of Weight, %.	Volatile Matter, %.	Acidity of Volatile Matter mg. KOH, %.	Sludge mg.	% Insol. in $CHCl_3$.	O_2 fixed gr.
A	930	2·69	0·855	2·400	100	188	47	1·54
			0·800	2·310	109	169	48	1·51
B	909	2·61	1·020	2·530	70	167	68	1·51
			0·955	2·420	88	153	54	1·46
C	881	1·54	1·315	2·520	117	123	54	1·4
			1·214	2·950	117	121	52	1·7
D	825	3·49	0·853	2·310	147	92	45	1·5
			1·400	3·040	128	108	35	1·6
E	912	6·81	0·995	2·26	77	264	90	1·3

Results per 100 gm. of oil.

In oils containing metallic soaps the latter are decomposed; the base of the soaps passes into the precipitable substances, which are thereby considerably increased.

Attempts to use catalysts, such as metallic copper and copper stearate, have shown that under the conditions of our tests these substances are ineffective.

Other tests, in which we used a so-called colloidal graphite, indicated:

1. Graphite acts as an anti-oxidant;
2. It no longer remains in suspension after being heated up to 300° C. This fact may possibly be attributed to the destruction of the substance used to stabilize its suspension.

These tests, which, as indicated at the beginning, are research tests, are still going on. In particular, we intend to make an exact balance of the oxygen, which implies the quantitative analysis of all the oxidation products: the volatile, the soluble and the precipitable. It is also our intention to complete the laboratory tests by trials in a special experimental engine in order to realize, as far as possible, the conditions of oxidation in the engine in practice. This is important, for it seems that our final aim—to adjust a test method to re-create the chemical reactions undergone by the oil in the engine—cannot be reached in any other way.

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[1] Maillard, Acker and Rengade, *Ann. des Comb. liq.*, 1936 (5), 945.
[2] For the technique see Maillard, Vellinger and Verdier, *Ann. des Comb. liq.*, 1932 (1), 7.
[3] Maillard, Acker and Rengade, *Ann. des Comb. liq.*, 1936 (6), 965.
[4] Levi, *Erdöl u. Teer*, 1933, p. 316.
[5] Orel, *Petrol. Z.*, 2.4.34.
[6] Maillard, *Congrès du Petrole, Paris*, 1937. See also Maillard and Friedrich, *Compt. rend. Acad. Sci.*, 18.10.37.
[7] Unpublished work. Effected at "Ecole du Petrole."
[8] Maillard and Edelberg, *Ann. des Comb. liq.*, 1936 (6), 1117.
[9] Maillard and Edelberg, *loc. cit.*
[10] Weiss and Maillard, *Ann. des Comb. liq.*, 1935 (3), 437. See also Maillard and Chibaeff, *C.R. Congrès Petr.*
[11] Vellinger and Muller, *C.R.*, 198, 1934, p. 2252; Muller, *C.R.*, 200, 1935, p. 1769.
[12] Maillard and Acker, *Ann. des Comb. liq.*, 1935 (3), 465.

INSTITUTE OF PETROLEUM.

THE One Hundred and Eighty-second Meeting was held on Tuesday, 10th May, 1938, at the Royal Society of Arts, John Street, Adelphi, London, when a paper entitled "The Changes Occurring in Lubricating Oils in Internal Combustion Engines," by Professor H. Weiss and Dr. A. Maillard, was discussed.

COL. S. J. M. AULD, O.B.E., M.C., D.Sc., President of the Institute, was in the Chair.

THE CHAIRMAN said that the present was quite an historic occasion, it being the first General Meeting of the Institute of Petroleum. The certificate of change of name had been granted, so that they must now call themselves by the official name of "The Institute of Petroleum." It was an important occasion for another reason, because they had the honour of having with them Professor Weiss, who was known personally or by reputation to most of them. They most heartily welcomed him that evening in coming to give his talk on a subject which was particularly connected with his name. To those who were not acquainted with Professor Weiss's designation, he was Professor in the Faculty of Science at Strasbourg University, and also Director of the École Nationale Supérieure du Pétrole.

PROF. WEISS then read the following paper: "Contribution to the Study of the Changes occurring in Lubricating Oils in Internal Combustion Engines" (see p. 407).

DISCUSSION.

THE CHAIRMAN said it had been a most impressive address, not merely because of Professor Weiss's obvious mastery of his subject, but also because of his mastery of the English language.

MR. C. G. WILLIAMS, Director of Research of the Institution of Automobile Engineers Research Laboratory, said he had not had the opportunity of studying the paper adequately, so that those observations which he would like to make would be somewhat disjointed, and would not do justice to the paper. In the first place, he thought that, from the standpoint of the automobile engineer, stability was one of the most important properties of a lubricant. Viscosity did not appear to be so necessary as was once thought; in fact, it was a positive nuisance at low temperatures, according to current advertisements. As one concerned with engine research, he had been brought up against those changes and deposits which occur in lubricating oils, and there was no doubt that great advantage would accrue if a test could be developed to indicate stability. There had so far been a general lack of success in this connection, but there was

no reason why such a test should not be developed, provided the conditions under which the oil worked in an engine were known, and reproduced in the test.

He felt in that connection that no one test was going to be adequate. Tests must cover a range of temperatures, since an oil had to experience temperatures from about 350° C. downwards. The test proposed by the author involved bubbling air through the oil sample, which appeared to be too severe a test, because it was generally understood that the Air Ministry and Indiana oxidation tests were open to criticism on the score that the oxidation induced by the bubbling of air or oxygen was too drastic.

He had been particularly interested in the question of deposits in engines from the standpoint of wear, and the Institution of Automobile Engineers had recently carried out some tests to study whether carbon deposits in the lubricating oil had a harmful effect on cylinder wear. They carried out the experiments on oil from the sumps of compression ignition engines. The oils contained approximately 3½ per cent. of carbonaceous matter and 0·1 per cent. of ash. Some of the oils showed no higher wear than new oil. One sample of used oil, containing about the same quantity of insoluble matter, gave, however, about eight times as much wear. It was found that the ash contained 42 per cent. silicon, as compared with 5·6 per cent. in the other oils showing the lower cylinder wear. The composition of deposits was, therefore, probably of more importance than their quantity.

The author had referred to the probability that oxidation of oil did not occur in the crank-case itself, and he apparently considered that the reason was associated with the absence of oxygen in the crank-case, whereas he (the speaker) thought it was due to the fact that the crank-case temperature was usually too low to cause oxidation. Professor Weiss quoted some tests, and concluded that it was possible for no air to be present in the crank-case. In some experiments which he (the speaker) made, the crank-case, etc., was carefully sealed, and various tests were carried out to make sure that there was no leakage of air into the crank-case. The gases accumulating in the crank-case were analysed, and the oxygen content never fell below 17 per cent. In other words, the gas leaking into the crank-case from the combustion chamber was largely air containing a small amount of unburnt or partly burnt fuel. In some other tests air was circulated through the crank-case, and the increase of oxidation was no greater than with no ventilation—*i.e.*, with the crank-case sealed.

He would refer to the author's test on an engine running on hydrogen. The I.A.E. did some similar tests, and were interested to note the cleanliness of the engine and oil at the end of the tests. The oil was certainly oxidized, but it had not lost its colour or become dirty, and it was concluded that, while the fuel might not have any effect on the rate of oxidation, it did have an effect on the appearance of the lubricant.

The author stated that the oil consumption of an engine was very largely due to mechanical leakage Apparently, his conclusion was based on some tests in which he ran an engine on hydrogen and analysed the exhaust gases for products of complete combustion. He (the speaker)

thought that Professor Weiss ought also to have analysed for hydrocarbons, since lubricating oil is not usually burnt completely.

Mr. A. T. Wilford (London Passenger Transport Board) said he felt that he had to differ from Professor Weiss in certain respects. He did not think that the author's method would help in finding out whether the fuel or the lubricant was a cause of contamination of an oil in a high-speed diesel engine. His (Mr. Wilford's) view was that in the case of an oil engine the contamination was due very largely to fuel. He would give some figures which related to the proportion of carbon and asphalt in the oil after use. By "carbon" he meant the portion of the suspended matter which was insoluble in benzene, and by asphalt the material which could be precipitated from the oil by petroleum ether after the carbon had been removed. He quoted the following figures for "carbon" and asphalt contents of oils after 12,000 miles use in six different engines, the differing carbon contents as compared with the relatively constant figures for asphalt being a sure indication that the former was due to fuel and not to lubricating oil :—

Engine No.	Carbon.	Asphalt.
1	6·93	0·44
2	12·08	0·46
3	7·10	0·52
4	8·18	0·40
5	6·68	0·49
6	6·76	0·39

The type of engine from which the samples were taken was now obsolete, and with better design of both head and injector nozzles, the "carbon" content of the used oil was about 1·5 per cent. after 6000 miles. This reduction can only be due to better combustion. That "carbon" was mainly produced from fuel rather than lubricant seemed also to be proved by the fact that the used oil from a direct-injection engine contained about twice as much as was found in oil from an indirect-injection engine. It should also be remembered that the amount of carbon in a used oil was influenced by oil consumption. All the lubricating oils to which reference had been made were of similar type, bought to the same specification, and very often the source of supply was the same. In the case of used oil from a high-speed diesel he had not found any method of differentiating between the carbon due to fuel and the carbon, if any, due to breakdown of the lubricating oil.

The last speaker made reference to what happened to the lubricating oil. With an oil engine, in order to ascertain the true fuel consumption it was a practice to take both fuel and lubricating oil consumed and add them together.

With regard to the periods during which oil was in use, figures could be given that were comparable with those quoted by Professor Weiss. In the concern with which he (Mr. Wilford) was associated it was the standard practice to change the lubricating oil at 12,000 miles. Taking the scheduled service speed as 12 m.p.h., they were using the oil for 1000

service hours. In one experiment three engines were run for as long as 37,000 miles without changing the oil, although one did not survive; that would be equivalent to 3000 hours' service. He would like to ask one question: in estimating viscosity, did the author take it on the used oil as it was received from the crank-case? He (the speaker) filtered it first. The fact that the viscosity of the filtered oil bore no relation to its "carbon" content was a further indication that the latter was not mainly an oxidation product.

Mr. R. Stansfield (Member) stated that the object of all the artificial ageing tests was apparently to distinguish between a good oil and a bad oil from the engine point of view, but it was not easy to say what was the point of view of the engine in every case. Oils containing metallic soaps showed a high ash. Presumably, in any ageing test which gave a high ash, the oil would be condemned, but there were diesel engines which would run between 3000 and 4000 hrs. using oils containing metallic soaps. The sludge content might be fairly high, but they would give no trouble. The same engines running on oils which passed the ageing test quite satisfactorily might fail in 300 or 400 hrs. This sort of thing made it very difficult to provide any generally applicable laboratory test for a lubricant.

He had selected an extreme case, but it prompted these questions: did the engine-builders take a large enough share in making the engines satisfactory for the lubricating oils? Was not the tendency too much to produce an engine good only in parts, and to encourage the designer to appeal to petroleum technologists for help, instead of insisting that the lubricant should be given just as much consideration as the other materials of construction? The oil had to take away a good deal of the heat, but was enough attention being paid to designing the engine piston and the combustion chamber so that they were symmetrical as regards temperature gradients thereby avoiding distortion of the seatings for the rings and reducing blow-by? Was enough thought given to possible means for increasing the amount of oil available to extract a given amount of heat, and so avoid local overheating of oil?

Too little emphasis was placed on the responsibility of the engine designer for many of the troubles generally ascribed to the lubricant itself.

Mr. E. A. Evans (Member) said that Mr. Williams had already apologized for those who had only a short time in which to peruse the paper. The paper was full of material, and was one which required careful study to obtain a concrete and logical picture of the author's views. Some of them might therefore obtain a slightly inaccurate interpretation of what the author wished to convey. They had admired his pluck in coming from Strasbourg and giving such a very delightful paper in good English.

Mr. Evans was interested to know whether Professor Weiss and some of his French associates were wedded to the use of chloroform. Was Professor Weiss really justified in reaching some of the conclusions from his results when using chloroform? Mr. Evans was not suggesting anything better, because he had been in the habit of using benzene. The

arguments in favour of benzene might be just as weak as for chloroform. Professor Weiss stressed the fact that as the oil became more and more used the portion insoluble in chloroform increased. Surely that was what one would expect, and the only interpretation which could be placed upon that observation was the natural one that as the products of oxidation from the oil become more and more oxidized, so they would become more and more insoluble. Professor Weiss had referred to the increasing insolubility of the material on the piston. Would it not be fair to suggest that, owing to the temperature gradation of the piston, the more oxidized material would be at the top—in fact in the hottest zone?

Mr. Wilford had referred to the method which he used to differentiate between carbon and asphalt. Unfortunately, there was a little danger in the use of the term "carbon," because it might imply the alternative term "soot." Years ago Mr. Evans thought that one might differentiate between asphalt and carbon by the use of benzene. It was quickly revealed by ultimate analysis that the idea was quite erroneous. The portion soluble in benzene might have an oxygen content of 8–20 per cent. of oxygen, whereas the portion insoluble in benzene might go up to 35 per cent. of oxygen. The insoluble portion was thus clearly not a carbon, but a much more highly oxidized material than the soluble portion. However, the deposits on the piston crown were not carbon, because they contained anything up to 20 per cent. of oxygen. He felt it a little difficult to reconcile these facts with the observation of the lecturer that the deposits on the piston head were the result of incomplete combustion of the lubricating oil. Perhaps the term "incomplete combustion" was a free translation of a French expression having a somewhat different interpretation.

Professor Weiss said that he would like to adopt an 8-hr. test. In England it would not be very popular. The 7-hr. test would be preferred, which would give one extra hour for heating the thermostat. Professor Weiss still adopted the air-blowing method, although admittedly he had modified it somewhat from the orthodox. Mr. Evans was not inclined to condemn air-blowing methods *ad hoc*, but as there were so many disagreements between the results of this type of test and the engine results, one's faith became a little subdued. The method used by the speaker was described in the paper on metal soaps in the *Proceedings of the General Discussion on Lubrication*, 1937. That method was probably worthy of further investigation, because it gave very indicative results with a large number of engine tests.

Mr. Stansfield had referred to a special oil containing metal soaps having peculiar properties. Mr. Evans thought that it was only fair to say that the metal soap referred to was aluminium. The aluminium soap did not appear to act as an inhibitor. Possibly its action was to prevent the adherence of deposit to the piston rings. Perhaps Mr. Stansfield could tell them whether aluminium soap had or had not increased cylinder wear when used in engine oils.

Dr. E. R. Redgrove (Member) said it was a great pleasure to him to congratulate Professor Weiss upon his paper and also upon his artistry, accidental perhaps, in withholding the proofs until that evening, because

if anything was likely to produce a healthy discussion, it was the question of lubrication, owing to the fact that the subject bristled with difficulties. In the trunk piston type of engine there were so many extraneous influences at work that it was almost impossible to follow what happened to the oil, and more often than not was the lubricant the victim of the conditions under which it operated.

The results which were obtained on the oil in the engine with the separate crank-case were very interesting, and particulars of the oil used and of the length of time it was in service would be helpful.

In spite of the experiments carried out with hydrogen as fuel, it had to be recognized that fuel carbon did, within wide limits, contribute to crank-case sludge.

The oxidation of lubricating oils followed many different courses, according to the type of oil itself and the temperature at which the oxidation occurred. Some oils rejected most of the carbonaceous material caused by their decomposition almost as soon as it was formed, whereas others held a large proportion in solution, and, generally speaking, of the solid decomposition products, asphaltic material was the first to be formed.

That more consideration should be given to the temperature at which oxidation tests should be carried out was a constructive suggestion, for whilst crank-case sludges could be easily removed by filtration, ring-sticking was one of the principal obstacles to the efficient operation of internal-combustion engines and none of the accepted oxidation tests seemed capable of indicating the behaviour of an oil under the varying conditions which were encountered in practice.

Admittedly both temperature and the nature of the oil itself had to be considered, and it would seem that examination of the residues left after a series of film evaporation tests at various temperatures would be a fruitful line of attack.

Some experiments carried out several years ago under his direction gave surprising results, and the information gained therefrom was most useful.

THE CHAIRMAN said they welcomed written contributions to the discussion, and he was going to tell Professor Weiss he could reply in writing to any part of it he wished and after having seen the questions in black and white. There had been some quite involved discussion, and they must remember that although members had had the pre-prints for only one day, Professor Weiss had had no pre-advice at all of members' remarks.

He would like to say a few words expressive of his own admiration of this type of work. The basic simplicity with which Professor Weiss and his colleagues were attacking the problem was impressive. It was producing facts which were bound eventually to lead to the truth, which was next to impossible from the speculations that were rife on the subject. Professor Weiss, like every man of science, would, he was sure, be only too willing to change his hypothesis as soon as a better one could be elaborated. That was the basis of scientific work. Any hypothesis was the correct one at a particular moment, but the horizon of truth was continually changing. That was what they had to remember in a big subject of this kind. If any conclusions could be reached which were logical, they should

be accepted, even though they were not necessarily those which would be accepted the day after to-morrow.

Some of the conclusions already come to had, however, borne the imprint of truth. The solubility of the products of oxidation appeared to him, for example, to be the correct way of attacking the problem.

Something similar to Professor Weiss's method he had recommended for use in conjunction with an Air Ministry Test carried out at elevated temperatures. It was well known that solubility decreases as the complexity of the ever hydrogen-poorer decomposition products increases. It would therefore seem to be of advantage to subject the oil to heat and oxidation—not until it contained a proportion of asphaltenes corresponding to a used oil in the crank-case, but until it turned into varnish-like materials such as deposit on piston skirts and valve seatings, or into solids such as gum up and coke piston ring grooves. The progressive insolubility of such materials in various solvents might indeed be very illuminating. They must remember that such materials were liable to vary very much in character with different kinds of oil and according to the operating temperature conditions of the engine. Ability, therefore, not only to withstand temperature but to give decomposition products of suitable fluxibility, would be of equal importance whether the deposits or varnishes were primarily formed from the lubricating oil or not.

In this same connection he ventured to think that the part played by low-temperature heat/oxidation in the crank-case was greater than the Professor implied. His own views were that there was the closest similarity between the heat and the heat/oxidation effect in the sequence of changes involved. There was little doubt that some of the polynaphthenic acids formed even in a turbine circulating system were of quite high molecular weight. The condensed nuclei formed by polymerization oxidation which seemed to compose the corresponding sludges and deposits were still more complex. It was worth noting incidentally that relatively little oxygen was called for in their elaboration.

It stood to reason that materials of this kind if formed in the crank-case and whether soluble in chloroform or not would decompose proportionately more quickly when they reached the cylinder by splash or otherwise. It was for this reason that he considered the conditions in the crank-case to be of at least equal importance to those ultimately responsible within the cylinder for the deterioration of the oil and the causation of damage.

Professor Weiss said that all the very technical questions could be much better replied to by letter, but there were a few words he wanted to say, because he had not made himself understood on basic principles. The apparatus was not an apparatus he was proposing for the test. He agreed with Mr. Williams that if they ever got to routine tests it would be testing without bubbling, but for the time being they had to compose their apparatus in that way in order to master it much more easily.

On the question of the influence of the fuel alteration of oil, it was known that there were many directions in which alteration occurred by the fuel, but when they wanted to study the alteration of the oil, they had to study the case where the factor would not come in because it would interfere with the experience they wanted to obtain.

As to the question of the incidence of temperature on metallic soaps, this was his answer: When they had metallic soaps they also had mineral oil, and before they could study the alteration they must know perfectly well what had happened to the mineral itself, and that was why they had left aside, except in some preliminary experiments, the question of the compounded oils. When they tackled the problem, some other factors would have to be considered—namely, mechanical properties of the sludge. It was quite probable that in certain soaps the sludge was a very good lubricant itself. For that reason the problem would become more complex, but it had not been tackled at all in the paper he had read.

Concerning the question of benzene and chloroform, benzene could be used if it were preferred: it would reach the approximation they were trying to get. The important fact was that both chloroform and benzene had shown the property of the sludge which had to be found out in the artificial ageing device. It was stated that the temperature had perhaps not so much influence as the length of time. There was the example of the piston which he gave—the piston which was quite black both at the top and the bottom. The time of heating must have been the same, and the bottom part was completely soluble in chloroform, and the top part insoluble, and the temperature factor therefore had a very important effect. Somebody said he could replace the effect of temperature by the effect of time. That recalled the interesting question, In how many centuries would a turkey be roasted at ordinary temperatures?

In the same way, a turbine oil, which will work for several thousands of hours in a turbine, will not produce sludge insoluble in chloroform; but if it is used to lubricate a motor-car engine, it will produce quite an appreciable amount within a few hours. So, generally speaking, you cannot replace the effect of temperature by the effect of time.

In the motor-car engine the oxidation of the lubricating oil takes place near the cylinder head; in the diesel engine the same occurs, and very often the crank-case oil is used to cool the inside of the piston. This explains the formation of sludge insoluble in chloroform.

THE CHAIRMAN moved a very hearty vote of thanks to Professor Weiss for coming to England to give them that remarkably fine address.

The vote was carried by acclamation.

C. H. BARTON (Member) wrote: I was particularly interested in the conclusions reached by Professor Weiss and Dr. Maillard regarding the decomposition of crank-case lubricants in the combustion space, since similar conclusions were reached by Mr. Thornycroft and myself in 1930 (*Aircraft Engineering*, Vol. 2, p. 109). I do not, however, consider that Professor Weiss is justified in dismissing the effect of fuel products, especially in diesel engines, in contaminating the crank-case oil in trunk piston engines (cf. Bouman II^e Congrès Mondial du Pétrole, Paris 1937, and I.M.E. Discussion on Lubrication, London, Oct. 1937, Vol. 1, p. 640).

Professor Weiss's assumption that the component of used oils which is insoluble in chloroform is entirely reponsible for crank-case deposits requires, I suggest, some modification. Actual sludge deposits which form in hollow crank-pins usually contain relatively small proportions of

chloroform-insolubles. Apart from oil and ash, the deposits contain appreciable proportions of asphaltenes (chloroform-soluble), which probably play a part in assisting sludge formation. Furthermore, practical experience shows that the chloroform-insoluble material in two used oils of different composition may be the same, and yet their tendency to form sludge deposits may be quite different. It seems, therefore, that oils differ considerably in their capacity for retaining sludge-forming materials in suspension or colloidal solution.

Mr. J. I. Hill (L.N.E. Railway) wrote: Professor Weiss has observed experimentally the progressive breakdown of lubricating oils used in internal-combustion engines, and finds that in the case of samples taken from the crank-case of marine (auxiliary) diesel engines (not fitted with filters) the amount of oxidation products precipitable by light naphtha increases regularly and is in proportion to the length of service.

He has observed similar behaviour of the oil in petrol engines; in the case of the 11-h.p. Renault engine he quotes figures substantially supporting his observations on diesel engines.

Thus, in the table on p. 412, the progressive increase in the amount of total deposit is shown to be fairly proportional to the distance run: the following figures taken from Professor Weiss' table on p. 412, together with averages, illustrates his point.

Number of Km.	Total Deposit, mg. per 100 cub. cm.	Average Deposit, mg. per 100 cub. cm. per 100 km.	Per 100 km. between Observed Periods.
611	108	17·7	17·7
1643	167	10·0	5·9
2834	280	10·0	9·6
4908	411	8·4	6·3
7045	611	8·7	9·3

The deposit observed at 600-km. run indicates an original high rate of production, but later, whilst there is a tendency for the rate of accumulation of the spirit-insoluble product to fluctuate markedly during successive periods of observation, yet the figures show a steady increase in the total amount of oxidation products produced in the oil with continued use.

Is it not a possibility that such behaviour might be a feature of a particular oil or oils, but not necessarily true for all oils?

In observations carried out on the progressive change in lubricating oil in petrol engines, it was found in some cases that the total spirit insoluble in the oil did not steadily increase with the progress of the run, and although there were fluctuations, yet with the particular engine and with at least four oils under test the total oxidation product, as indicated by the material precipitated by petroleum spirit, was shown not to increase steadily with the progressive run, but to be maintained within fairly narrow limits at a constant figure for considerable periods.

In this particular series of observations, two similar engines were under observation: they were Dorman 40-h.p. 4-cylinder engines with cast-iron pistons. They were fitted to locomotives carrying out shunting opera-

tions: it is not possible to give the mileage run, but the hours of operation were carefully observed.

In our tests a sample of oil was taken from the crank-case regularly each month, care being exercised to see that the samples were taken immediately after the engine had stopped work: as far as possible, samples were not taken immediately after fresh make-up oil had been added. The oil capacity of the sump at working level was 2½ gals.

The laboratory examination of the samples of oil consisted first of precipitation by petroleum ether (boiling range 60–80° C. A.R. quality; "Aromatic-Free"): the same spirit was used throughout the tests. The precipitate was filtered and weighed, and this is quoted in the tables below as "total amount precipitated."

The precipitate was then completely extracted with hot benzene (crystallizable); the benzene removed from the extract and the residue weighed: this is quoted below as "soluble in benzene."

The insoluble was then ignited and the ash weighed: the difference is quoted as "insoluble in benzene"; ash figures are also quoted.

In Test *A* the oil used was a high-grade proprietary brand of motor oil; the trial ran for 26 months, during which time the oil was not changed, but the working oil level was made-up as required. The capacity of the sump was 2½ gals., and during the trial period the total addition of new oil amounted to 61 gals.; from the additions of new oil, it was calculated that the consumption of oil was 0·13 pint per hour of work.

The following figures are extracted from the full records; weights are in grammes per 100 gm. of oil:—

Hours of Work.	Total Insoluble (Precipitated by Petroleum Ether).					% Insoluble in Benzene Calculated on Organic Matter.
	Grm. per 100 gm.	Average per 100 hrs. Work.	Make-up.			
			Ash.	Soluble in Benzene.	Insoluble in Benzene.	
0	—	—	—	—	—	—
137	0·30	0·22	0·20	0·10	—	—
685	0·26	0·038	0·05	0·04	0·17	80
1096	0·35	0·032	0·05	0·10	0·20	67
1503	0·32	0·021	0·06	0·11	0·15	58
2055	0·25	0·013	0·05	0·05	0·15	75
2603	0·24	0·01–	0·05	0·02	0·17	89
3082	0·32	0·011	0·04	0·04	0·24	86
3288	0·41	0·013	0·07	0·04	0·30	88
3425	0·52	0·015	0·10	0·08	0·34	81
3562	0·55	0·015	0·09	0·09	0·37	81
Average (24 samples)	0·38	—	0·06	0·08	0·24	—

It will be seen that up to about 3000 hrs. the total insoluble showed no signs of regular increase, and the upward trend did not show itself until about 3300 hrs. running.

In Test *B*, on a similar engine doing similar work but for fewer hours

per day, the oil was again a high-grade proprietary brand, marketed throughout the country.

The following table gives typical results extracted from the full records :—

Hours of Work.	Total Insoluble (Precipitated by Petroleum Ether).	Average per 100 hrs. Work.	Ash.	Soluble in Benzene.	Insoluble in Benzene.	% Insoluble, Calculated on Organic Matter.
0	—	—	—	—	—	—
81	0·73	0·9	0·24	0·07	0·42	86
324	0·83	0·26	0·40	0·15	0·30	70
688	0·63	0·1	0·18	0·11	0·34	76
972	0·69	0·07	0·09	0·10	0·50	83
1296	0·69	0·05	0·20	0·05	0·44	90
Average	0·68	0·053	0·23	0·11	0·34	—

Here the total insoluble after nearly 1300 hrs. running is actually less than at 81 hrs., and remained practically unchanged from about 500 hrs. running to the end of the trial, although there were fluctuations in its composition.

It should be added that fuel dilution remained fairly constant throughout the length of the trials, and the results given were therefore not influenced by the dilution.

Other tests on petrol engines of lorries doing delivery work with very limited mileage have yielded similar results.

It is unnecessary to quote detailed figures : in the table below are given details of two other trials ; the average results on all samples tested during the period of observation are quoted, and those of the last sample examined. It will be seen that the figures for the last sample do not show any marked difference from the average.

In this test a proprietary brand of oil was used.

Vehicle No.	No. of Samples Examined.	Mileage.	Average Analysis of all Samples.				Last Sample Examined.			
			Total Insoluble.	Ash.	Soluble in Benzene.	Insoluble in Benzene.	Total Insoluble.	Ash.	Soluble in Benzene.	Insoluble in Benzene.
1	8	4393	0·72	0·07	0·12	0·53	0·61	0·07	0·05	0·50
2	8	3180	1·27	0·09	0·20	0·98	1·34	0·07	0·08	1·19

In another test on a lorry engine, using a solvent refined oil, the following figures were obtained :—

Time.	Total Insoluble.	Ash.	Soluble in Benzene.	Insoluble in Benzene.
6 mths.	0·65	0·05	0·05	0·55
12 „	0·75	0·06	0·10	0·59

From the results it would appear that in certain circumstances and with certain oils the total insoluble matter precipitated by spirit from the used oil does not increase proportionately with the length of service.

On the other hand, some tests have revealed a steady increase in the accumulation of products precipitated by petroleum ether. In the following table are given figures from a trial of a heavy motor oil in the engine of a 30-cwt. lorry.

Weeks in Use.	Total Insoluble (Precipitated by Petroleum Ether).					% Insoluble in Benzene Calculated on Organic Matter.
	Total.	Average gm. per Week.	Make-up.			
			Ash.	Soluble in Benzene.	Insoluble in Benzene.	
0	—	—	—	—	—	—
2	0·29	0·145	0·10	0·04	0·15	79
4	0·44	0·11	0·05	0·03	0·36	92
8	0·90	0·11	0·07	0·07	0·76	91
12	1·35	0·11	0·07	0·13	1·15	90
15	1·53	0·10	0·09	0·16	1·28	89

Do not these results indicate that the increase of spirit-insoluble products in used oil varies with the oil, in some cases progressively increasing with the run, as indicated by Professor Weiss, and in other cases attaining a maximum in the early stages of running, with only small variation from that figure for comparatively long periods?

If that be so, then it seems to indicate that only certain constituents in the oil are susceptible to oxidation changes, and the behaviour of the oil in service is dependent on the proportion of such constituent.

These results are consistent with the conclusions of Auld as to the susceptivity of mineral lubricating oils in use, that "the bulk of evidence points to the changes in used oil only affecting a comparatively small proportion."

In reply to the Discussion, PROF. H. WEISS wrote:

In reply to Mr. C. G. Williams.

I should like to repeat, in the first place, that the aim of my lecture was not to describe and propose a new reception test for lubricating oils. The apparatus mentioned in the latter part of the paper is the one which seemed to us the most appropriate to fulfil our experimental scheme in the research field which we have indicated.

Several measurements have shown that the atmosphere of the crank-case loses a certain proportion of its oxygen. This loss can occur:

(*a*) either because the oil combines with a certain amount of oxygen (without formation, at the temperature of the crank-case, of a deposit insoluble in chloroform or hot benzene), or

(*b*) because, at the moment of the combustion of the fuel in the cylinder, a certain amount of the air of the crank-case is driven by a blow of the combustion gases, which contain only very little oxygen.

The absence of gaseous hydrocarbons and of carbon monoxide in the escape gases in measurable amounts has been shown by analysis; but quite

an appreciable quantity of oil, in very thin suspension in the escape gases, has been condensed.

In reply to Mr. Wilford.

The viscosity has always been measured on filtered oils. After short runs the viscosity had never varied much. But such has not been the case after tests of long duration (1200 hours in diesel motors on ships).

In the long duration tests, with crank-cases containing small amounts of oil, you must take into account the oil consumption. In the case of some locomotive diesel engines the oil consumption after 12 hours amounted to 20 per cent. of the oil contained in the crank-case. We can realize that after several hundred hours' service the oil has been replaced many times.

In reply to Mr. Evans.

Comparative tests have been made with hot benzene and chloroform at ordinary temperature. The results of the analysis were practically the same.

We have adopted chloroform because experience has shown us that we had more accidents by fire than by sleep.

We have observed that the amount of oxidation products increases with the time of running; but the proportion insoluble in chloroform remains practically constant.

We are convinced that the temperature gradient along the piston is the cause of the differences in solubility of the oxidation products along the piston head.

By " products of incomplete combustion of the oil " we mean the products of oxidation at high temperature.

Concerning the duration of the experiments, 8 hours is quite convenient for us, *i.e.*, 4 hours in the forenoon, 4 hours in the afternoon; the apparatus is left running alone for 2 hours at lunch time.

In reply to Dr. Redgrove.

Three oils have been used. All were called " Diesel Oil Medium heavy "; but we had no indication concerning their origin. Their densities at 20° were = 0·906, 0·915, 0·9215.

In reply to Col. Auld.

We fully agree on the manner in which a working hypothesis, such as the one of the present paper, has to be used and adjusted, or even completely left aside when the experimental work is progressing in the study of such complex phenomena.

We have not studied systematically, in the present work, the important problem of ring-sticking. We only made a short reference to it in stating that we noticed the simultaneous presence of formaldehyde and phenol in the escape gases, the combination of which leads to the formation of bakelite.

We quite agree on the possibility of the formation of slightly oxidized bodies from the oil in the crank-case, the decomposition of which in the hottest spots of the motors will lead to deposits insoluble in chloroform. Experiments in that direction are running in our laboratory.

In reply to Mr. Barton.

In the case of the Marine Diesel Engines quoted, there could be no dilution by the fuel of the oil in the crank-case, because of the design of the motors. Distillation under high vacuum of the oil after 1200 hours running has confirmed the absence of fuel in the lubricating oil. This example seems conclusive to us, demonstrating the existence of an alteration of the oil independently of the dilution by the fuel in the cases in which the latter takes place.

We have said that the part of the deposit which is insoluble in chloroform is also insoluble in the hot oil; we agree also on the point that chloroform-soluble deposits are also found in the crank-case sludge. It seems obvious that all the deposit which is insoluble in the oil contributes to the formation of the sludge. We must not forget that if a given oil will give different results in two different motors, all the oils have not the same dissolving power on the deposits obtained by precipitating with normal petrol. For instance, a naphthenic-base oil will dissolve these deposits much better than a paraffinic-base oil.

In reply to Mr. Hill.

We meant to say that the amount of precipitable matter increases always, but not that it must be proportional to time of running. At first, if the sample of used oil is taken too soon after an important addition of new oil, you can have results smaller than on the preceding sample.

On the other hand, the lowest level reached by the oil before the refill is of importance.

For these reasons, and for many others, we cannot expect, in the case of motors the crank-cases of which contain small amounts of oil, a strict proportionality. Moreover, we cannot compare the results of tests of small duration, in which the oil has not been renewed several times, with those of tests of 3560 hours in which the oil has been renewed twenty-three times. In the long-duration tests, with crank-cases of small capacity, we think the phenomenon occurs in the following way. At the beginning there is an increase in the amount of oxidation products, the oil level falls; we refill with new oil. Thus the concentration in oxidation products becomes smaller; then, the concentration increases again, and so on. It seems clear that in these conditions—*i.e.*, if the duration of the test is long and the consumption of oil important—the concentration in oxidation products will quickly reach a limit, which will depend on the way the fresh oil is added. This limit is not reached in a test of small duration.

It seems to us quite certain that oils of different constitutions will not behave in the same way from the point of view of the accumulation of sludge. The dissolving power of the oil varies greatly from one case to the other.

But we think that experience has proved that an oil cannot be considered as a mixture, a few constituents only of which can be altered, or that an oil can be regenerated several times and that its tendency to alteration has not decreased.

THE DETERIORATION OF TURBINE AND TRANSFORMER OILS IN SERVICE.*

By W. Francis, M.Sc., Ph.D., F.I.C., and K. R. Garrett, B.Sc.

Much work has been published on the deterioration of lubricating and insulating oils in service, but investigators appear to have concentrated mainly on the measurement of changes in physical properties, rather than on the investigation of the nature of the chemical changes taking place. This note is a small addition to the literature on the chemical aspects of the problem, and relates particularly to the deterioration of turbine and transformer oils. These oils are considered together, since they normally operate under similar low-temperature conditions, precluding the possibility of cracking taking place with the liberation of free carbon.

The changes generally considered to occur in practice are, first the introduction of oxygenated groupings into the oil molecules, followed either by the cision of simple fatty acids, leaving unsaturated molecules which readily polymerize, or by direct condensation with associated molecules via the oxygenated groupings, to form new products of high molecular weight. These heavy products precipitate out in favourable circumstances, especially in the presence of water, as emulsions or sludges.

When emulsions or sludges are found to any extent, turbine oils are generally discarded, on account of the danger to the machine that would arise should the sludge cause blocked oil-pipes, seized bearings or unsatisfactory governing.

The development of acidity unaccompanied by heavy sludging is not considered very serious either in transformer oils or in turbine oils, for it does not appear to reduce appreciably the dielectric strength of insulating oil, whilst the lubricating properties of turbine oils are actually improved by the presence of carboxylic and hydroxylic groupings, according to well-established practice and theory. Oils are therefore only discarded on account of high acidity when this causes excessive corrosion of vital parts.

It appears of importance to be able to examine the nature and amount of the oxygenated groupings introduced into oil molecules by low-temperature oxidation processes.

The B.S.I. tests for oils are of some assistance in following the course of these changes, since the general result of oxidation at low temperatures is to increase viscosity, specific gravity, Conradson value and acidity. Except for acidity, such changes are not great for low degrees of oxidation, so that oxidation must be considerable before the B.S.I. tests give definite indications of change. The standard acidity determination lacks precision and is unsuitable for a detailed investigation of this nature. The standard procedure may, however, be greatly improved by the use of a different indicator than the one postulated. This is phenolphthalein, which changes at pH 8–9 from colourless to pink, a change which is most difficult

* Paper received July 21st, 1938.

to see owing to the red colour prevailing in oxidized oils and the yellow colour of the alcohol–water–salt emulsion produced during titration. The use of thymol blue, with titration exponent at pH 8·8 and a change in colour from yellow to blue, gives the endpoint with greater precision in most unfavourable lights.

A further improvement, at least from a research standpoint, is to titrate electrometrically. One method of doing this, using the glass electrode for measurement of pH, has been described recently (Rolfe and Alcock, *J. Soc. Chem. Ind.*, **56** (1937), 294). We have confirmed that reasonably sharp end-points and good agreements can be obtained by this method, and three typical curves are given in Graph I. The peaks in the curves for rate of change of pH when titrating used turbine and transformer oils occur at values pH 9·0–9·5, indicating the very weak nature of the acids present.

Both these modifications in the B.S.I. method do not, however, remove the inherent defect of the determination—namely, that the value obtained is lower than the true value by an irregular amount dependent on the partial solubilities of oil oxidation products in alcohol, alcohol–water and alcohol–salt–water mixtures. During the initial digestion with alcohol the organic acids present become distributed between the alcohol and oil in proportion to their specific solubilities and to the amounts of alcohol and oil present. As titration proceeds, with neutralization of a portion of the acids already extracted from the oil, the equilibrium is displaced and more acid tends to be dissolved from the oil by the alcohol. Since, however, water is being continuously added to this alcohol, the acidic products become decreasingly soluble, and, in cases where acidity is very high, appreciable quantities of acid remain in the oil at the end of the titration, and are not estimated. The results obtained by direct titration of the oil–alcohol mixture are, therefore, always lower than the true acidity figure. This can be obtained by repeated extractions with alcohol and separation of the alcoholic extracts before titration, summating the results obtained. An example of this method of procedure is given in Table I, which shows the acidities obtained by extracting 10 gm. of oil with four successive lots of 50 ml. of alcohol.

TABLE I.

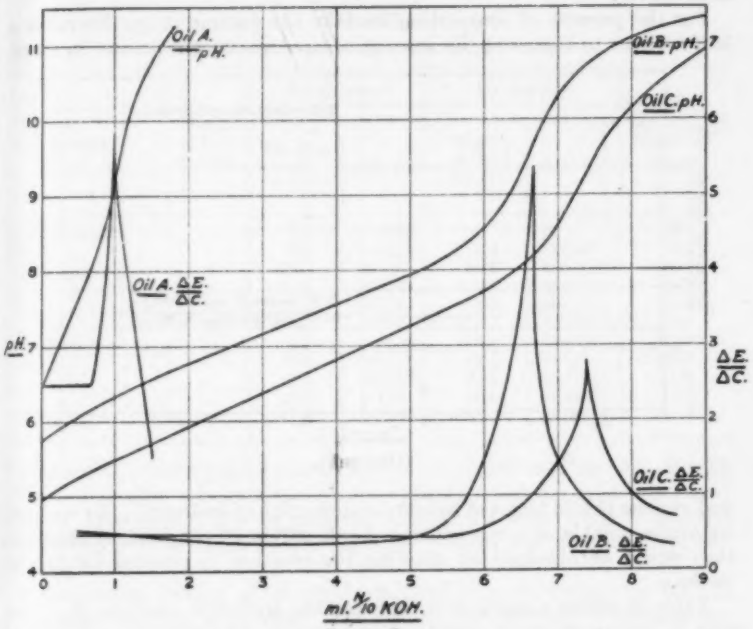
Acidity of Oxidized Oil by Exhaustive Alcoholic Extraction.

	Ml. 10*N*-KOH per 10 grs. Oil.	
	Titration to Thymol Blue.	Electrometric Titration.
Extract I	6·7	6·65
„ II	1·15	1·03
„ III	0·26	0·28
„ IV	0·20	0·05
Totals . . .	8·31	8·01

The higher results obtained with thymol-blue indicator are due to slightly over-shooting the true end-point in each titration. The actual value given

by the B.S.I. method (modified by the use of thymol blue as indicator) was 7·58 ml. of KOH, and by titrating electrometrically was 7·4 ml., as shown in Graph I, curve C. Curve B, in Graph I, represents the potentiometric titration of the first alcoholic extraction of the above oil.

The differing pH values of the alcoholic extracts of oxidized oil suggest that significant information regarding the nature of the strength of the acids extracted may be obtained from such figures, but the results so far obtained have been conflicting and disappointing. Attempts have also been made



GRAPH I.

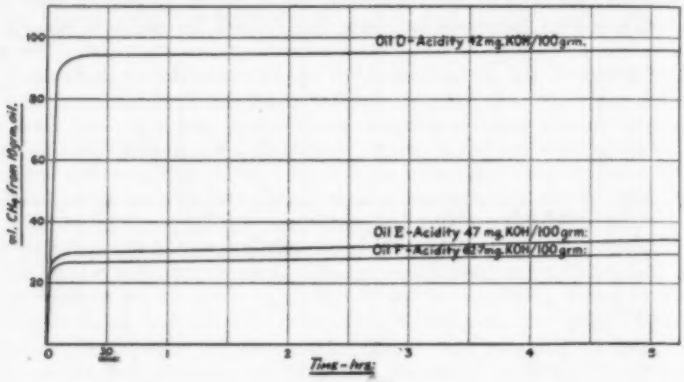
to determine directly the so-called pH of oxidized oils using non-aqueous solvents by methods used industrially in connection with the trade examination of materials such as boot polish, furniture cream, etc. The solvents tried have included trichlorethylene, xylene, butyl alcohol and xylidine, but, although apparently reasonable readings were obtained spasmodically, they were difficult to reproduce, and we have come to the conclusion that such methods are useless. In such work the readings of the potentiometer appear to be affected by oil films forming on the glass electrode, by static currents set up during stirring and by the state of wetness or oiliness of the ground-glass joints to the potassium-chloride bridge.

Some light is thrown on the nature of the oxygenated groupings by the application of Stadnikoffsky's method for determining reactive hydrogen groupings using the Grignard reagent. The method we have developed is to dissolve a known weight of oil in xylene, dried over sodium, and to add

to this mixture, in a Lunge nitrometer, an excess of amyl magnesium iodide. On shaking, a large proportion of the total volume of methane recoverable is immediately released, the remainder being slowly liberated, as will be seen from Graph II.

The Grignard reagent reacts with all the oxygenated groupings introduced into the molecule, whether they are in the form of carboxyl, hydroxyl, aldehyde or ketone. Where these groupings are protected by steric hindrance, or are present in extremely complex molecules, it may react more slowly.

For the purpose of comparison we take the volume of gas liberated in half an hour to represent the amount of reactive oxygen present in an oil,



GRAPH II.

and express this in terms of weight or proportion of hydroxyl. By so doing we arrive quickly at a reproducible result within 10 per cent. of the value that would be obtained by allowing the reaction to proceed for several weeks.

Table II shows a comparison between the hydroxyl contents of certain oils, in various stages of oxidation, as determined by the Grignard method and as calculated from the acidity determinations by the improved B.S.I. method.

It will be seen that the amount of oxygen present in used oil is very much greater than would be expected from consideration of the acidity determination alone. The ratio of hydroxyl groupings as acidity to total oxygen as hydroxyl varies in any oil with the degree of oxidation. In the case of the turbine oil shown in Table II this ratio increases from 3·7 per cent. when mildly oxidized to 18·4 per cent. when highly oxidized. It should be emphasized that these figures relate to oil of one type, and that wide variations may be expected in these ratios when examining oils of different origin. For example, it will be seen from Table II that the transformer oils examined, although of intermediate acidity, contain a much greater proportion of the total hydroxyl as acidity than the turbine oil. The fact that the ratio of hydroxyl as acidic groupings to total hydroxyl increases with the degree of oxidation, indicates that oxygen at first

attacks reactive groupings without the formation of acidic residues, and that in time rearrangements take place with the production of acidic formations in the oxidized oil molecules. It may also be inferred that the more highly refined transformer oils are relatively free from readily oxidizable groupings, since oxidation tends to go direct to acidic groupings without the formation of the intermediate relatively acid free oxygenated compounds.

The use of the Grignard reagent enables new light to be thrown on the possibilities of reclaiming methods for oils that have deteriorated in practice.

TABLE II.

The Determination of Oxygenated Groups in Oils.

Sample.	Stage of Oxidation.	By Grignard.		By Acidity.		OH as Acid / Total OH × 100.
		Ml. Gas at N.T.P.	OH, %.	Mgms. KOH/100 grm. Oil.	OH, %.	
New turbine oil .	—	2·0	0·0152	0	0	0
Used " " .	1	9·7	0·0739	8·9	0·0027	3·7
" " " .	2	17·7	0·135	34·7	0·0105	7·8
" " " .	3	21·0	0·160	45·3	0·0137	8·7
" " " .	4	22·4	0·170	64·9	0·0197	11·6
" " " .	5	92·2	0·702	425	0·129	18·4
Transformer oils .	—	1·8	0·0137	10·6	0·0032	23·4
" " .	—	14·8	0·113	89·2	0·0271	24·0
" " .	—	17·0	0·1294	94·6	0·0321	24·8
" " .	—	16·6	0·127	98·0	0·0297	23·2
" " .	—	17·3	0·1317	138	0·0418	31·7

For example, after repeated extractions of the above-used turbine oil with alcohol, a residue was obtained almost entirely free from acidic and oxygenated groupings. The oxygenated compounds were actually isolated as dark-coloured resinous bodies when the alcohol was distilled from the extracts.

By extracting 100 gm. of the highly oxidised oil seven times with alcohol, we obtained 11·5 gm. of extract. The residue gave 18·5 ml. of methane per 10 gm./residue with the Grignard reagent, and had an acidity equivalent to 23·5 mg. KOH/100 gm./residue, whilst the corresponding figures before extraction were 94 c.c. methane per 10 gm. of oil and 424 mg. KOH per 100 gm. of oil.

In other words, 82·5 per cent. of the total reactive oxygenated groupings and 94·5 per cent. of the total acidity were removed by the alcoholic treatment. After this treatment the oil was clear-bright, a pure orange colour, agreed well with the standard test figures for the original oil and deposited no sludge on standing when exposed to light. The treatment was therefore completely successful in removing most of the oxygenated products from the oil, and the reclaimed oil appears to be as good as new, when judged by appearance and the usual tests. In fact, it seems reasonable to suppose that the residue is more stable to oxidation than the original oil, since groupings liable to attack in the original oil have been removed by the practical refining process of oxidation followed by removal of the oxidized products from the system. Alcoholic extraction, therefore,

is an effective method of reclaiming deteriorated turbine oils, although there may be difficulties in the way of its commercial application.

The same type of result is obtained by treating a highly oxidized oil with active earth, although the effect is not so pronounced as with exhaustive extraction by means of alcohol. By digesting the above oil with 5 per cent. by weight of Fuller's earth for 24 hours and filtering the residue, we obtained a reduction of 19·5 per cent. in acidity and 31 per cent. in activity towards the Grignard reagent. This treatment, although less complete than extraction with alcohol, appears to remove the principal sludge-forming materials present, since the treated sample has remained bright and free from sludge on exposure to light over a period of several years. Many other oxygenated oils that we have treated in this way from time to time have remained bright on standing, whereas previously they have sludged heavily in a few days. The active-earth treatment is, of course, well known, and has been used in practice, but we believe that the use of the alcohol extraction in this connection is novel.

22, *Cambridge Avenue,*
New Malden,
Surrey.

THE TEMPERATURE-SENSITIVITY OF VISCOUS OILS.*

By D. J. W. Kreulen (Member).

It is well known that certain viscous oils are temperature-sensitive—that is to say, the results of tests, in which the viscosity of the oil is of importance, are dependent on the temperature to which the oil is heated before the test. This has been pointed out by several investigators in connection with the A.S.T.M. pour-point.[1]

Phenomena similar to those occurring at the pour- and setting-point also appear in the viscosity of these oils if the latter is determined at relatively low temperatures. It is therefore necessary, in measurements of viscosity, always to indicate to what temperature the oil has been heated before the experiment.[2]

In the same way, results of the pour test are very dependent on the temperature to which the oil is heated before cooling. With different degrees of pre-heating from 50° to 100° C., differences of 20—30° C. in pour point can be found. B. H. Moerbeek and A. C. van Beest[3] have given an explanation of this phenomenon. After stating that distillates, unlike residues, are not temperature-sensitive, they regard the asphaltenes present in the residues as responsible for the phenomenon. In explaining the shape of the temperature–pour-point curves they remark :

"The most plausible explanation of the above-mentioned action of the asphaltenes is that, on cooling from a sufficiently high temperature, they become concentrated on the surface of the crystals. This impedes the formation of larger crystals (not of aggregates), but the chief result of this 'skin' of asphaltenes is that the paraffin-wax crystals retain much less oil, and cannot form a network of crystals so easily, which reduces the pour-point. The asphaltenes, moreover, seem somewhat to retard the process of crystallization. There is an artifice by means of which one can remove the asphaltenes from the paraffin wax and thus rule out their effect on the pour-point. This is by cooling from 100° C. to 0° C., and then heating to about 35° C. and again cooling; one thus, indeed, achieves the object in view; at 35° C. the main mass of the wax crystals has already dissolved, whilst the 'skin' of asphaltenes from which the paraffin wax has been largely or wholly eliminated are obviously left behind in a state in which they cannot be 'picked up' by the crystals separating out during the second cooling."

Thus the ascending part of the curve is explained by the melting out of ceresine (the skin-forming asphaltenes remaining conglomerated so that they are not able to exercise their pour-point depressing action), and the declining part by the destroying of asphaltene-skins at higher temperatures, so that they, in the then dispersed state, are able to join the crystal surfaces, opposing thereby the formation of large crystal units.

* Paper received January 28th, 1938.

The above-mentioned theory was able to give an explanation of phenomena stated by Kolvoort, Moser and Verver [4] in their study on the separation of paraffin-wax from oil in a dewaxing process. Nevertheless we want to mention in this paper some experiments carried out at our laboratory, in order to give a contribution to the subject and to show that in some cases an explanation can also be approached from another point of view.

The conception "asphaltenes" not being a singular one, we have to realize that what is flocculated or, perhaps, more exactly, coacervated [5] by a solvent of low surface tension (either pentane, as used by some investigators, or special petroleum spirit, as is common in asphaltic matter determinations) can be separated into :

(*a*) Lightly adsorbed oils, which can be easily removed by refluxing with petroleum spirit (substance α).

(*b*) Paraffin and ceresine, which can be removed by refluxing with alcohol (substance β).

(*c*) The remaining asphaltic matter consisting of solid particles covered with strongly adsorbed protective oils which make it possible to disperse them in liquids of a sufficient high surface tension (substance γ).[6]

If we call the oil freed from the coacervated phase δ, then oil containing asphalt is represented by $\delta + (\alpha + \beta + \gamma)$, the part $(\alpha + \beta + \gamma)$ being coacervatable.

In our experiments we have not only studied the influence of the asphaltenes as a whole, but, moreover, that of the mentioned components α, β and γ separately.

The experiments were carried out with the oil mentioned in Table I.

TABLE I.

Oil.	% Asphalt (DIN. D.V.M. 3660).	Viscosity in Centistokes at :		
		30° C.	40° C.	50° C.
A . . .	6·13	—	166	87
B . . .	1·25	185	85	48
C . . .	0	180	21	13

The viscosity was determined after bringing the oil to the mentioned temperature, carefully avoiding preheating. Now, by treating with pentane, petroleum spirit and alcohol, the following oils were prepared:

Coacervating with Petroleum Spirit :

$$A_1/B_1(\delta + \gamma + \beta)$$
$$A_2/B_2(\delta + \gamma)$$
$$A_3/B_3(\delta)$$

Coacervating with Pentane :

$$A_4/B_4(\delta)$$

The Original Oils :

$$A_5/B_5/C_5$$

As the A.S.T.M. pour-point requires about 50 c.c. of oil, an I.P.T. setting-point determination was carried out, so modified, however, that it was possible to test small quantities of oil. The apparatus employed is given in Fig. 1.

After placing 5 c.c. of the oil in tube U (diameter = 10 mm.), this tube was preheated in a water-bath to the desired temperature. It was then placed in the air until the temperature of 30° C. was reached after which

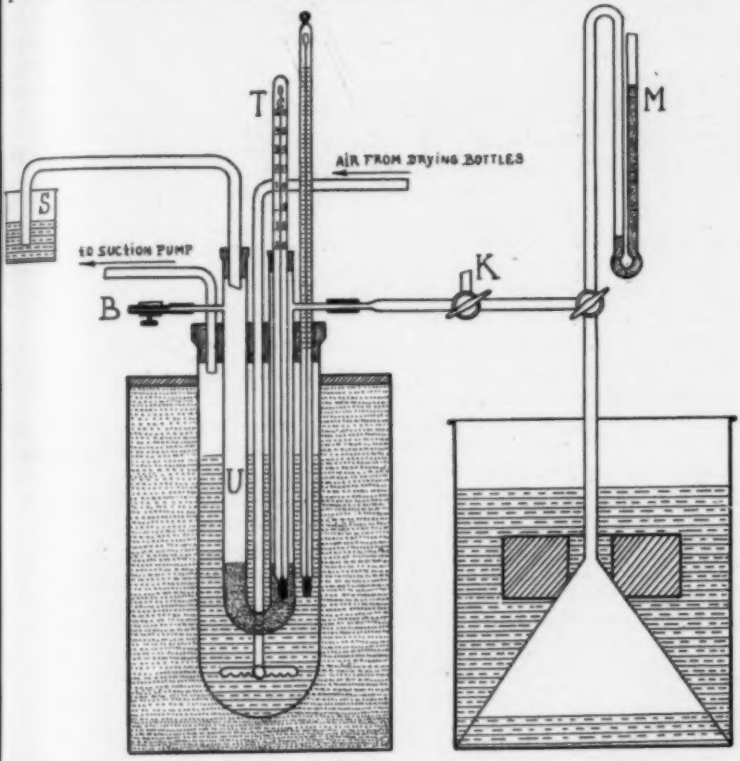


FIG. 1.

it was placed in a wide test-tube, the latter well insulated with glass-wool from the surrounding air. At the beginning of the test this test-tube was filled with ether at 30° C. By sucking air through the ether a regular cooling amounting to 1° C./minute could be realized (from + 30 to −15°/C.). After each degree of temperature fall (measured in the oil) a pressure of 75 mm. water was exerted on the oil in the right-hand arm of the tube. The oil was then pressed into the left-hand arm, if liquid, and consequently the compressed air was forced to escape from the tube S (3½ mm. diameter, dipping 1 cm. into gas oil).

The temperature at which the air-bubble needed more than half a minute

for loosing itself from the end of the tube was taken as a criterion. In order to avoid stirring the oil while testing, only one bubble was allowed to escape. Then both the left-hand arm and the right-hand arm of the U-tube were brought into communication with the air, so that the oil could resume its original level.

The figures given in Table II were collected in the tests.

TABLE II.

Preheated to :	30° C.	35° C.	40° C.	45° C.	50° C.	60° C.	70° C.	80° C.	90° C.	100° C.
Oil *A*1 . . .	17	19	21	22	28	28	21	16	14	14
„ *A*2 . . .	13	12	12	15	18	19	13	5	6	5
„ *A*3 . . .	2	3	4	2	3	3	3	3	3	2
„ *A*4 . . .	14	12	15	14	13	16	16	15	13	14
„ *A*5 . . .	16	15	16	17	15	− 3	− 2	−11	−11	−11
„ *B*1 . . .	12	13	17	22	25	2	5	4	9	9
„ *B*2 . . .	11	14	18	21	24	0	− 2	− 3	− 2	4
„ *B*3 . . .	13	14	7	− 2	− 5	− 3	− 4	− 4	− 4	− 3
„ *B*4 . . .	13	10	8	9	9	11	11	10	11	11
„ *B*5 . . .	10	13	14	16	13	4	−21	−21	−21	−21
„ *C*5 . . .	23	24	25	26	27	25	20	11	3	− 7

In Figs. 2, 3 and 4 the setting-points are indicated in a graph as a function of the temperature of preheating.

From the graphs it is evident that a tendency to temperature insensitivity is apparent if an oil is freed from the coacervatable phase by pentane (lines *A*4 and *B*4). This has already been stated by Moerbeek and van Beest. The same tendency was indicated by oil *A* after treating with petroleum spirit (*A*3). However, oil *B*, treated in exactly the same way, gave a decidedly temperature-sensitive product (*B*3). Also the asphalt-free oils *A*1, *A*2, *B*1, *B*2 and *C*5 are no doubt temperature-sensitive. The asphaltenes without asphalt are thus able to create the phenomenon, and it is therefore necessary to realize that, when we accept the idea of asphaltene-skins and melting-out phenomena, these conceptions should not be estimated too literally. This was well realized by Moerbeek and van Beest, since they put the expression "asphaltene-skins" between quotation marks.

That the asphalt itself, the solid phase with strongly adsorbed protective oils, cannot be regarded as responsible follows from Table III, in which

TABLE III.

Oil.	% Asphalt.	Max. Drop of Temperature in Curve.
*A*5 . . .	6·13	28° C.
*B*5 . . .	1·25	37° C.
*C*5 . . .	0	34° C.

the drop of temperature, stated for the tested oils, is compared with the asphalt content.

Moreover the phenomenon is not specific for mineral oils, for it can be demonstrated with honey. It is well known that the honey gathered by

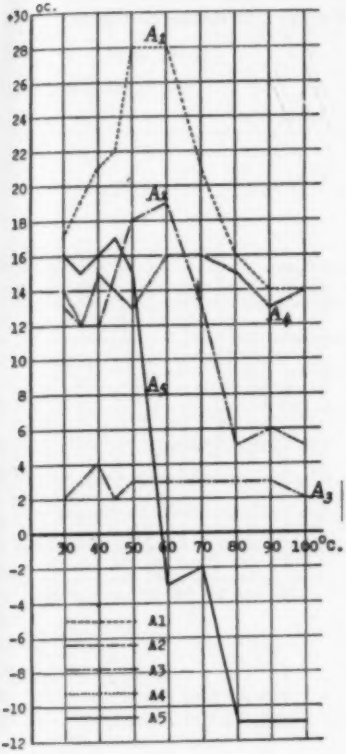


FIG. 2.

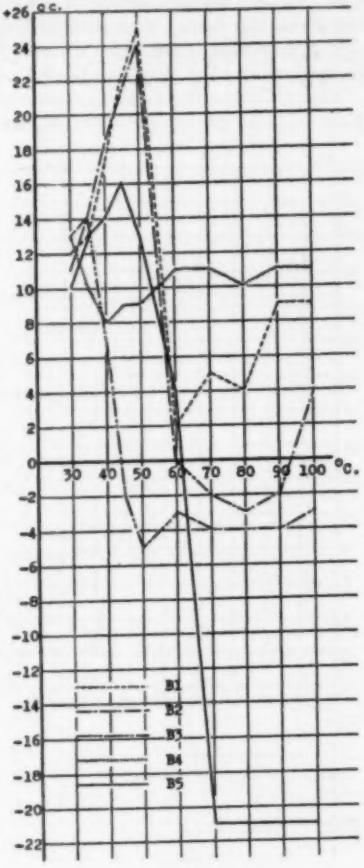


FIG. 3.

the bee on *Calluna Vulgaris* is thixotropic. We are struck by the similarity of the properties of honey and thixotropic oils, and a sample of honey was therefore tested in our apparatus (Table IV, fig. 5).

TABLE IV.

Preheated to :	30° C.	35° C.	40° C.	45° C.	50° C.	60° C.	70° C.	80° C.	90° C.	100° C.
Honey . . .	6	8	15	17	7	8	7	17	11	14

The honey curve shows two maxima: one at 45° C. (the temperature at which the maximum is shown by mineral oils) and one at 80° C. Now, at 80° C. the disappearance of wax particles was observed, these being present as the honey was removed by ourselves out of the comb. It is very remarkable that this second maximum also coincides with the disappearance of a disperse phase.

Other thixotropic substances were also investigated, as for example iron oxide sol, but no temperature sensitivity of the setting-point curve was

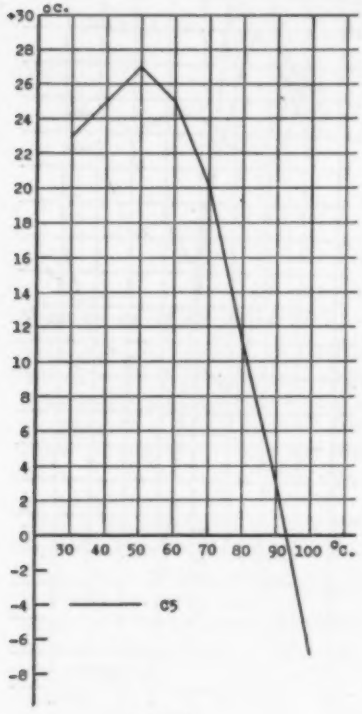


FIG. 4.

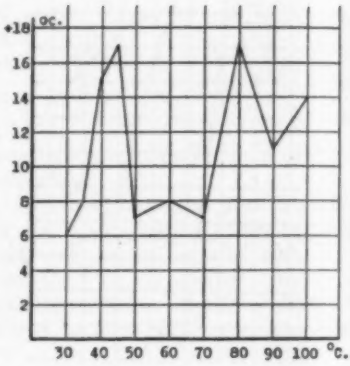


FIG. 5.

found. It seems that the phenomenon is exclusively limited to systems in which crystallization occurs.

It is also, however, restricted to systems with a high viscosity. Thus with gas-oils no temperature sensitivity can be found, even after the addition of asphaltenes. It was therefore necessary to ascertain if the phenomenon would disappear with declining viscosity.

Oil *A*5, practically insensitive in the asphaltene-free state (*A*3) (setting-point then at about + 3° C.) was therefore diluted with gas-oil of about the same setting-point (+ 2° C.). The asphaltene-free oil *A*3 was not influenced in setting-point by the addition of the gas-oil (Table V).

The original oil *A5* was also diluted with the same quantities of gas-oil and the setting-point curves were determined (Table VI, Fig. 6).

TABLE V.

Preheated to :	30° C.	35° C.	40° C.	45° C.	50° C.	60° C.	70° C.	80° C.	90° C.	100° C.
Gas-oil . . .	2	—	2	—	2	—	—	2	—	2
Oil *A3* . . .	2	3	4	2	3	3	3	3	3	2
67% *A3* + 33% gas-oil . . .	3	2	2	3	1	1	1	1	1	1
33% *A3* + 67% gas-oil . . .	3	—	1	—	1	1	—	1	—	1

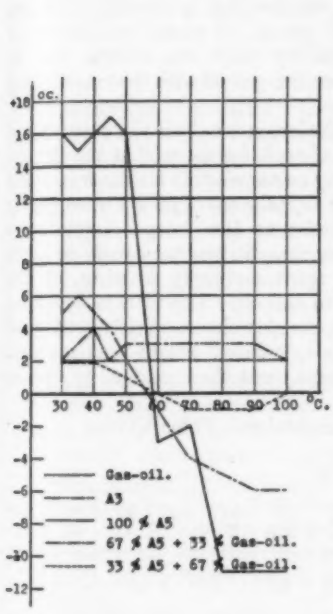


FIG. 6.

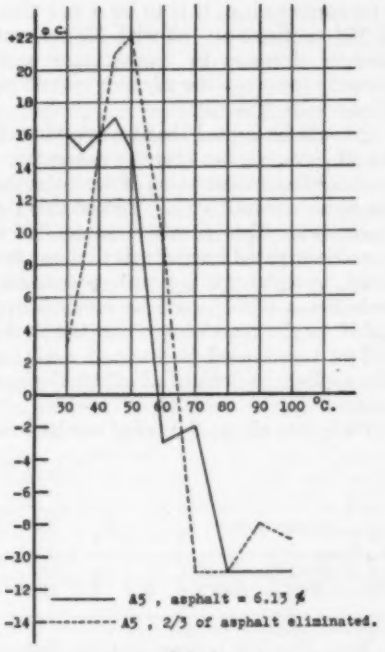


FIG. 7.

TABLE VI.

Preheated to :	30° C.	35° C.	40° C.	45° C.	50° C.	60° C.	70° C.	80° C.	90° C.	100° C.
A5	16	15	16	17	15	−3	−2	−11	−11	−11
67% *A5* + 33% gas-oil . . .	5	6	5	4	2	−1	−4	− 5	− 6	− 6
33% *A5* + 67% gas-oil . . .	2	—	2	1	0	−1	−1	− 1	− 1	0

The viscosity of the mixtures is given in Table VII.

TABLE VII.

Oil.	Viscosity at:	
	40° C.	50° C.
*A*5	166	87 c.st.
67% *A*5 + 33% gas-oil . . .	38	24
33% *A*5 + 67% gas-oil . . .	12·6	9·1

Thus it is evident that viscosity is a most important factor in influencing the temperature-sensitivity of an oil.

In consequence, it is to be noted that the first fall in viscosity (original oil 166 centistokes; oil with 33 per cent. gas-oil, 38 centistokes) causes a stronger decrease in temperature sensitivity than the second fall in viscosity (compare the mixture with 33 per cent. gas-oil with that containing 67 per cent. gas-oil).

It could be argued that by applying dilution, not only is the viscosity of the oil changed, but also the percentage of asphaltenes, so that the diminution in the concentration of the latter may be responsible for the weakened temperature sensitivity. To test this the asphaltenes of oil *A*5 were partly eliminated. This involved some difficulties as the "dry" asphaltenes once coacervated are difficult to disperse again. It was eventually brought about by coacervating with petroleum spirit and only filtering off the asphaltenes which could be removed from the oil. The filtrate was then added to the remaining oil in the flask, the petroleum spirit distilled off and at last heated in vacuum until the calculated weight was reached. The asphalt content of oil *A*5 (6·13 per cent.) was then reduced to 2·3 per cent.

With this oil the following results were obtained (Table VIII).

TABLE VIII.

Preheated to:	30° C.	35° C.	40° C.	45° C.	50° C.	60° C.	70° C.	80° C.	90° C.	100° C.
Oil *A*5 (6·13% asphalt)	16	15	16	17	15	−3	− 2	−11	−11	−11
Oil *A*5 (2·3% asphalt)	3	8	15	21	22	9	−11	−11	− 8	− 9

From Fig. 7 it is clear that the observed phenomenon, after diluting with gas-oil, can in no way be attributed to the diminished asphaltene content of the oil.

Very remarkable were the results obtained by inoculating. These experiments were started as we inclined more and more to the view that retarding crystallization in consequence of the viscous medium would represent a most essential factor in the phenomena studied. Should this be true then it could be expected that inoculation with a small quantity of the original oil would raise the setting-points which were found on preheating (solution of all the crystals present) at 100° C. Consequently the oils *A*5, *B*5, *C*5 and *B*2 were tested after preheating at 100° C. The

oil was then again preheated at the same temperature, but when, during the subsequent cooling, the temperature of 40° C. was reached, a small piece of copper thread, provided with a loop at the end, was dipped lightly in the original (not preheated) oil and then moved through the oil in the U-tube both in the right-hand arm and the left-hand arm. The test was then carried out in the usual way after cooling to 30° C. The figures collected in Table IX were obtained.

TABLE IX.

Oil.	After Preheating at 100° C.	After Preheating at 100° C. followed by inoculating at 40° C.
A5	−11	0
B5	−21	+12
C5	− 7	+25
B2	+ 4	+20

The results obtained by these inoculation tests make it very probable that merely ordinary crystallization phenomena are involved. The fall of the curve above 50° C. may be explained by a normal retardation of crystallization. That the asphaltenes, as far as they are viscous, can improve the phenomenon is evident. Moreover, it is true that these asphaltenes contain paraffin and ceresine, and it is very probable that it is particularly the crystallization of these substances which is involved, for if they are brought into true solution, by raising the temperature, but not above 50° C., the phenomenon is strengthened. However, crystal nuclei are still present then, by inoculation or by heating up to below 50° C. If these crystal nuclei are absent as a result of heating above 50° C., a retardation of crystallization shows itself in a very low setting-point—that is to say, under-cooling. In practice this is also of importance, as, when realized, it becomes clear that the minimum pour-point is rarely attainable, since traces of crystalline matter will very probably always be present in practice (as in pipe-lines and in bunkers), which will prevent under-cooling. This, however, does not obviate the fact that in practice the oil will be readily pumpable at temperatures below the maximum pour-point, as this last constant only represents a certain yield value which in the laboratory test is very different from that involved in pumping conditions.

It was interesting to investigate if the temperature of maximum setting-point agreed with the temperature of complete solution of the paraffin and ceresine crystals. Now, according to Einstein, in a disperse system an equation $\eta_s = \eta_0 (1 + a\,\zeta)$ holds, wherein η_s is the viscosity of the dispersion and η_0 that of the dispersion medium, ζ is the volume of the dispersed particles and a is a constant.

Thus the viscosity of a dispersion is greater than that of the pure dispersion medium, and becomes all the greater with increasing volume of the dispersed particles.

It is true that in asphalt containing oils we are dealing with a disperse system. The volume of the asphalt itself must, however, be considered as a constant. According to the above formula, a disperse phase disappears

on heating the oil, for if we plot log . log(V_k + 0·8) against the log of the absolute temperature, as proposed by Ubbelohde, in the case of temperature-sensitive oils we do not get straight lines. This is demonstrated by Fig. 8.

From this figure it appears that a disperse phase slowly disappears on

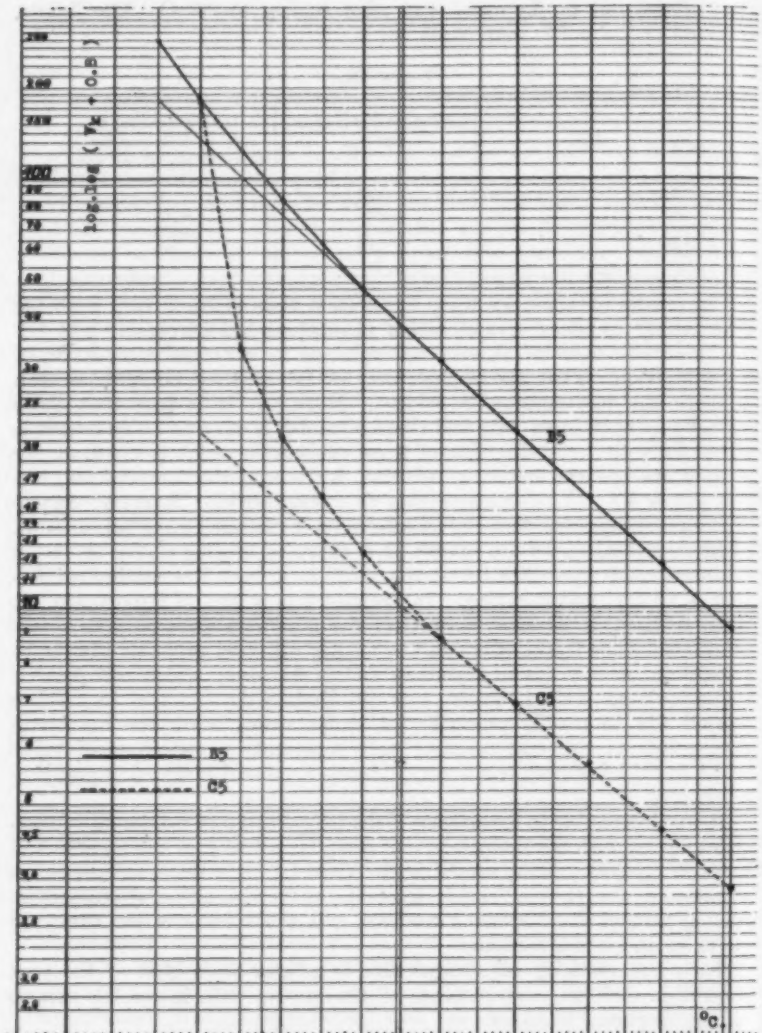


FIG. 8.

raising the temperature to about 50° C. Above this temperature the lines are straight, indicating that either no disperse phase or a constant (in our case asphalt) disperse phase is present.

Since the maxima in the setting-point curves are found at approximately the temperature at which complete solution of paraffin and ceresine occurs, it seems very possible that in this range of temperature the maximum concentration is reached. On the other hand, the last traces of crystal nuclei are the cause of the supersaturated solution, obtained by cooling during the experiment, crystallizing as a fine network through the whole of the mass. In this way a relatively stable network of very fine crystals is formed.

We were able to demonstrate this on a mixture of 100 per cent. paraffin-hydrocarbons obtained by the Berginization of paraffins of high molecular weight. The product consisted of a light oil in which paraffin crystals were suspended. If this product was heated at a temperature below that of complete solution of paraffin crystals, then, by slowly cooling, crystallization occurred in such a way that a liquid was obtained with loose crystals lying at the bottom. The supernatant liquid was quite clear, but if heating was applied until complete solution of the crystals occurred : then, by cooling, a relatively stable network of fine crystals throughout the whole of the liquid was formed, rendering it an apparently solid mass. In these experiments a retardation of crystallization could not occur, the liquid not being viscous.

It therefore seems to us that the rise and fall of the pour-point curves is readily explained in this way, and does not require the postulating of asphaltenes acting as pour-point reducers as an explanation.

It is of interest to mention a typical example of the retardation of crystallization at the pour-point test. A paraffin-containing residue without asphalt showed the maximum pour-point of 40° C. This residue was diluted to obtain a mixture of lower viscosity.

With 75 per cent. of a gas-oil, having a viscosity of 21 centistokes at 20° C., a mixture was obtained with a viscosity of 56 centistokes at 20° C. This mixture had a maximum pour-point of + 8° C.

The same residue was then diluted with 75% of a gas-oil having 7 centistokes at 20° C. A mixture with 23 centistokes at 20° C. was thus obtained having a maximum pour-point of + 14° C.

Both gas-oils had a very low pour-point (below −15° C). We see from these experiments that the mixture with the lowest viscosity showed the highest pour-point; no doubt in that mixture the retardation of crystallization was less.

Laboratory for Oil- and Coal-Chemistry,
" Glückauf,"
Rotterdam.

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THE PRINCIPLES OF SOLVENT DEWAXING. PART III: EQUILIBRIA AND COMPUTATIONS FOR DOUBLE SOLVENT SYSTEMS.

By M. Ba Thi, B.Sc., A.I.C. (Student Member), T. G. Hunter, Ph.D., A.R.T.C., A.I.C. (Member), and A. W. Nash, M.Sc., M.I.Mech.E. (Member).

In the two previous papers [1, 2] of this series equilibria representations and computations for dewaxing processes employing both single solvents and solvent mixtures completely miscible with the oil at the operating temperature have been described. The computation methods discussed in the second paper [2] were of limited applicability in so far as they applied only to a special case of double solvent equilibrium, and also could not be used when the ratio of the two solvents in the solvent mixture was 1 : 1. An alternative method of computation free from these limitations has been devised for the double solvent mixture, where both solvents are completely miscible with the oil at the dewaxing temperature, and is presented here.

Since the publication of the two papers, referred to above, a certain amount of discussion has appeared in the literature [3, 4, 5] with regard to these methods and their applications. The significance of these methods and the general applications of the diagrams are considered and described at the conclusion of this paper.

Equilibrium in a Four Component Solid–Liquid System.

In the previous paper [2] representation of equilibrium in a four-component system was obtained by the means of a space-model of a regular tetrahedron. An alternative method of representation for this system by a space-model of an equilateral triangular prism may also be employed.

Fig. 1 shows such an equilateral triangular prism in perspective, the angles *A*, *B*, *C*, and *D* of which represent the respective pure components of a four-component system *A*, *B*, *C*, and *D*. The six possible binary systems are given by the lines joining the angular points, with the exception of the lines *AA* and *BB*, any point on which always represents pure *A* and pure *B* respectively. The binary system *AB* is represented by the two lines *AB*. The four possible ternary systems, *A–B–C*, *A–B–D*, *A–C–D*, and *B–C–D* are given respectively by the lower and upper triangular surfaces and by the right and left rectangular surfaces. The remaining surface *ABAB* at the rear of the prism represents the binary system *A–B*. All possible quaternary mixtures may be represented by points inside the space enclosed by the five boundary surfaces.

Any cross-section of the figure represents the equilibrium state of some special quaternary system. The top of the prism—namely, triangle

ABD—represents the equilibrium state of the ternary system *A–B–D*, while the bottom triangle *ABC* represents the ternary system *A–B–C*. The cross-section *ABM* represents the equilibrium state of the quaternary system *A–B–C–D* in which the ratio of *C*/*D* is constant at the value *DM*/*MC*.

A model of equilibrium relationship for the case of one solid and three liquid components forming a two-phase system at some temperature below the melting point of solid *A* and above the freezing points of the liquids

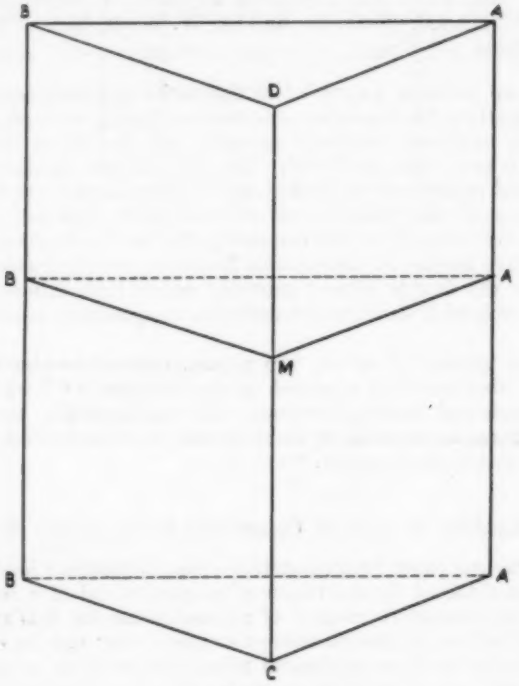


Fig. 1.

B, *C*, and *D* will take the form of Fig. 2, two views of which are illustrated—the complete model in 2 (*a*) and a sectioned model in 2 (*b*).

In Fig. 2 the saturation surface *bdcb* is shown as if it were a plane surface. Actually the saturation surface *bdcb* is not a plane, but takes the form of what can best be described as a propeller-shaped surface as illustrated in Fig. 3. For ease of drawing it has been shown as a plane surface in Fig. 2.

In Fig. 2 the points *b*, *b*, *c*, and *d* on the edges *AB*, *AB*, *AC*, and *AD* represent, respectively, the solubilities or saturated solutions of solid *A* in liquid *B*, liquid *C*, and liquid *D*. The curves *bc*, *cd*, and *bd* represent, respectively, the solubilities or saturated solutions of solid *A* in the liquid

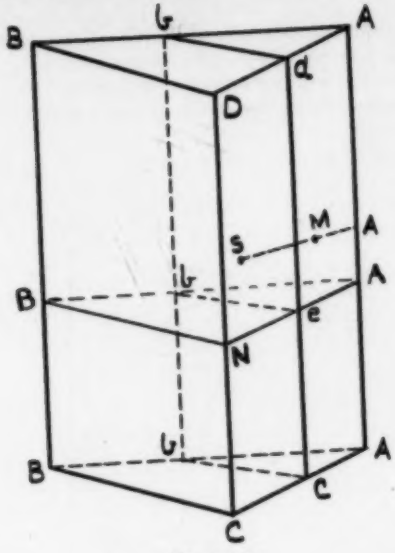


FIG. 2 (a)

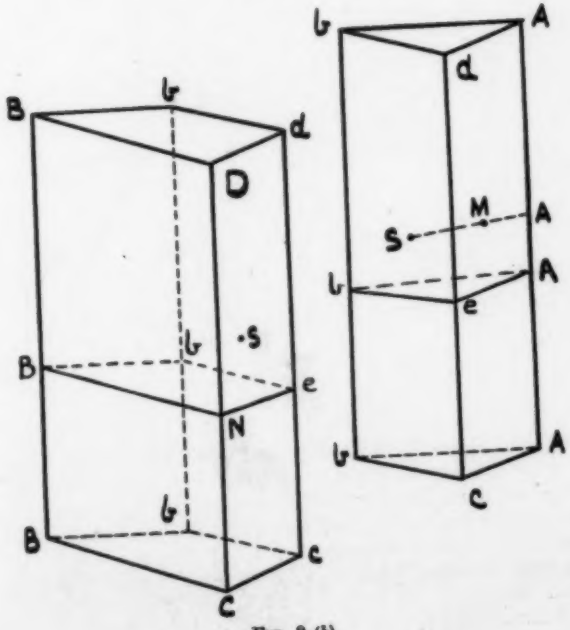


FIG. 2 (b)

mixtures *B–C*, *C–D*, and *B–D*, and are ternary saturation curves. The quaternary equilibrium is represented by the surface *bdcb*. Each point on *bdcb* represents a saturated solution of solid *A* in the liquid mixture *B–C–D*. Any mixture the composition of which may be represented by a point within the space *BDCBbdcb* is an unsaturated liquid, and exists as a single homogeneous liquid phase. Any mixture the composition of which may be represented by a point within the space *AAbdcb* must separate into

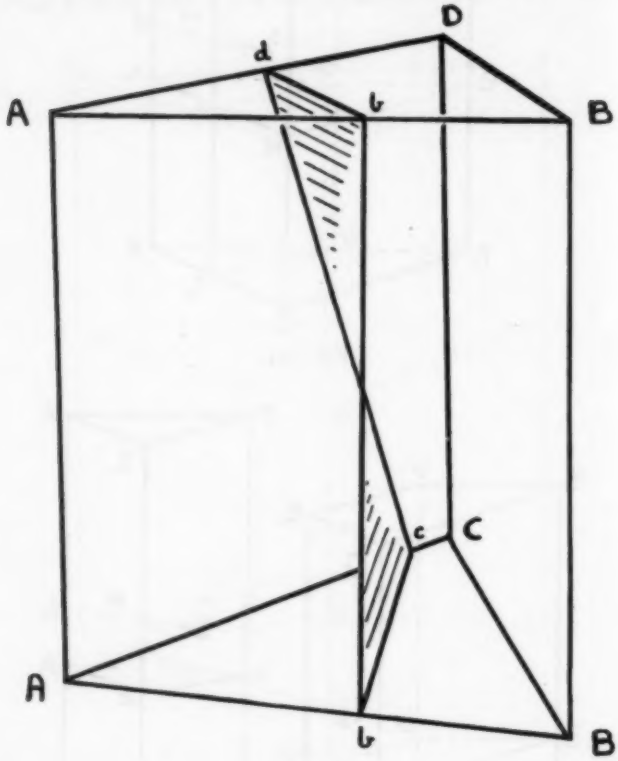


FIG. 3.

two phases, solid phase *A*, and a saturated liquid phase with a composition represented by a point on the saturation surface *bdcb*. A mixture represented by point *M* in Fig. 2 would separate into solid *A* and a saturated liquid of composition represented by point *S*. The ratio of solid *A* to liquid *S* would be given by the ratio *SM*/*MA*. The line *AMS* is therefore a tie-line joining the two phases, solid *A* and liquid *S*, which are in equilibrium.

A perspective drawing, as in Fig. 2, affords only a qualitative description

of equilibria. It is better therefore to work with a projection of the prism on a plane in which plotting may be carried out quantitatively. The most convenient is the orthogonal projection, in which the prism and the space figure within it are projected upon the base plane by means of parallel lines perpendicular to the base.

In Fig. 4 the projection of the quaternary saturation surface of Fig. 2 on to the base plane *ABC* is illustrated. Point *d'* is the projection of the point *d* and the line *bd'* is the projection of the line *bd*. The line *bc* is, of course, already on the base plane *ABC*.

In Fig. 2 the line *be* is the equilibrium line for the system *A–B–N*, where *N* is a mixture of *C* and *D* in the ratio $C/D = DN/NC$. Where the lines *bd*, *dc*, *cb*, and *bb* are straight lines it can be shown geometrically that $DN/NC = de/ec$. The projection of the line *dc* of Fig. 2 is the line *d'c*

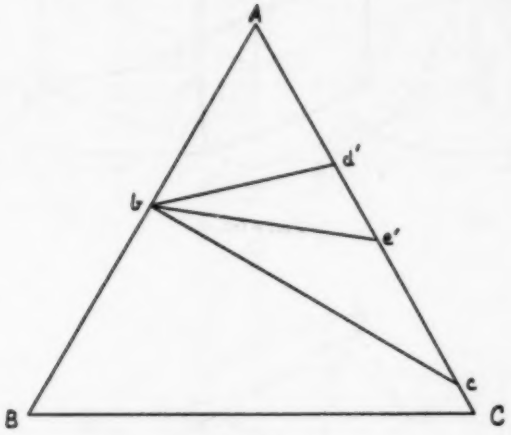


FIG. 4.

of Fig. 4. The projection of *e* can then be easily located on Fig. 4 as the point *e'*, where $d'e'/e'c = DN/NC$. The line *be'* of Fig. 4 is the projection of the line *be* of Fig. 2, and represents equilibrium in the system *A–B–C–D*, where C/D is kept constant in the ratio DN/NC. For the case where the saturation curves in the ternary systems *A–B–C*, *A–B–D*, and *A–C–D* are straight lines, this method may be employed for obtaining the equilibrium relationships in the quaternary system *A–B–N*, where *N* is any solvent mixture of *C* and *D*. Where any of the ternary saturation curves have only a small curvature, the method may again be used without the introduction of serious error.

In the type of equilibrium under consideration three out of the four possible ternary systems are two-phase systems. The case described above in connection with the prism method of representation, and also described in Part II [2] of this series in connection with the tetrahedron method of representation, is actually a special case where the equilibrium data in the three two-phase ternary systems were represented by straight lines.

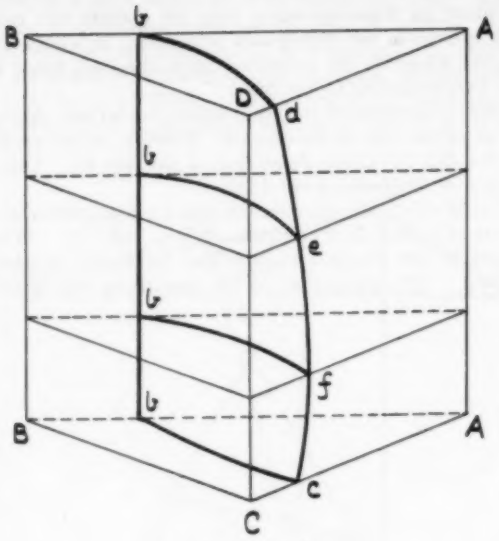


FIG. 5 (a).

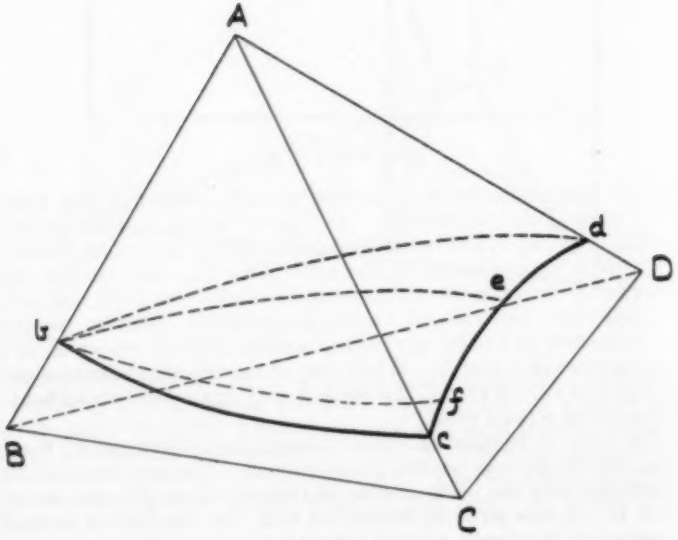


FIG. 5 (b).

This special instance very seldom occurs in practice, although the case in which two out of the three two-phase ternary systems are represented by straight lines, whilst the third is represented by a curve approximating to a straight line, appears to be of fairly frequent occurrence in dewaxing operations. This latter instance may be most conveniently treated as an example of the special case. Perhaps the most usual case is for one or more of the three two-phase ternary systems to be represented by a curve.

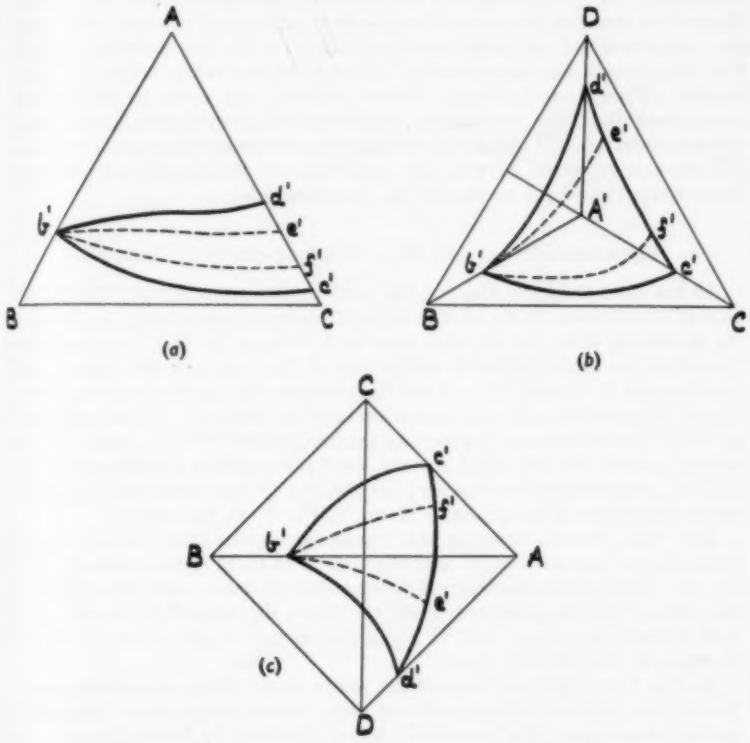


FIG. 6.

An equilibrium treatment somewhat different from that already described elsewhere [2] and above is then necessary. This type of equilibrium will be discussed here for the completely general case, where all three two-phase ternary systems are represented by curves, for both the prism and tetrahedron representational methods.

Equilibrium for this general case represented on both prism and tetrahedron models is illustrated in Fig. 5 (*a*) and (*b*) respectively. Here the equilibrium in the two-phase ternary systems *A–B–C*, *A–C–D*, and *A–D–B* is represented by curves, and the saturation surface *bcd* or *bdcb* is a curved

surface. The lines *be* and *bf* are lines of constant solvent–solvent ratio and, where in the special case previously described these were straight lines, they are now curves.

The projection of the prism and tetrahedron models of Fig. 5 is shown in Fig. 6, on which both the two usual projections of the tetrahedron appear as 6 (*b*) and 6 (*c*). In these diagrams *b'd'* and *b'c'* are the projections of the saturation curves *bd* and *bc*, whilst *b'e'* and *b'f'* are the projections of the constant solvent–solvent ratio lines *be* and *bf*. In the special case previously considered the projections of the constant solvent–solvent ratio lines, themselves straight lines, were straight lines, and could be easily drawn by the constructional methods described above or in the previous paper.[2] For this general case these constant solvent–solvent ratio curves cannot be located by any purely constructional method, but must be determined experimentally. For any single equilibrium diagram describing a double solvent system it will usually be sufficient to determine three such constant solvent–solvent ratio curves, any other curves being interpolated from these as required by a method to be described later.

Equilibria in an Oil-Wax Solvent–Solvent System.

As has been shown in the two previous papers, approximate representation of equilibrium in an oil-wax solvent–solvent system may be obtained by assuming that the oil and wax each behave as single components. Therefore by replacing solid component *A* by wax and the three liquid components *B*, *C*, and *D* by oil and the two solvents, approximate representation of equilibrium in the desired system is obtained. The equilibrium at 80° F. for the system Burma wax (melting point 108° F.), Anglo-Iranian second cooled blue oil, ethyl acetate and light naphtha (boiling point 100–120° C.), represented by the two projections of the tetrahedron and the single projection of the prism, is shown in Fig. 7 (*a*), (*b*), and (*c*).

The data for constructing the quaternary saturation surface for the wax–oil–ethyl-acetate–light naphtha system of these figures were obtained by the cloud-point method. The equilibrium data were determined at the rather high temperature of 80° C., where the saturation curves are of well-defined curvature, and in consequence the whole system is a good example of the general case.

In Fig. 7 (*c*), the projection of the prism model of representation, only a few of the constant solvent–solvent ratio curves shown were obtained by actual experiment, the remainder being obtained by interpolation. The method of interpolation employed for this purpose is a useful and convenient method of extending experimental data, and is described in detail below.

In Fig. 8 the curves *AB*, *AC*, *AD*, and *AE* represent equilibrium curves for the system wax–oil–solvent/solvent at T° F. projected from a solid prism model. In this projection, which is similar to that of Fig. 7 (*c*), *W* represents pure wax, *O* oil, and *S* represents either pure solvent S_1 or pure solvent S_2 or a solvent mixture of S_1 and S_2.

AB is the equilibrium curve for the system wax–oil–solvent S_1, whilst *AC* is the equilibrium curve for the system wax–oil–solvent S_1/S_2 where $S_1/S_2 = a/b$ and *AD* is the equilibrium curve for the system wax–oil–solvent S_1/S_2, where $S_1/S_2 = c/d$. *AC* and *AD* are therefore two constant

solvent–solvent ratio curves. *AE* is the equilibrium curve for the system wax-oil–solvent S_2.

Point *P* divides *OS* in the ratio *PS*/*OP*, so that oil/solvent = *PS*/*OP* = *e*/*f*. The line *WP* intersects the four equilibrium curves at *G*, *H*, *I*, and *J*.

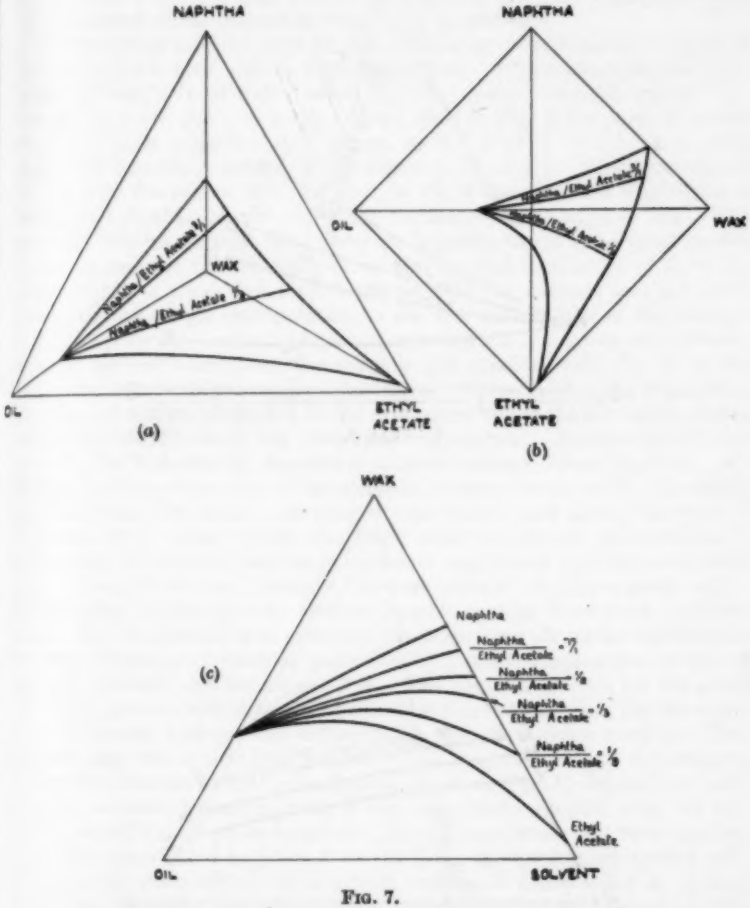


FIG. 7.

G represents the solubility of wax in a mixture of oil and solvent S_1 when oil/S_1 = *e*/*f*. *H* represents the solubility of wax in an oil double-solvent mixture composed of solvent S_1 and solvent S_2 in the ratio of S_1/S_2 = *a*/*b*, and when the oil/solvent mixture ratio = *e*/*f*. Finally, point *J* represents the solubility of wax in a mixture of oil and solvent S_2 when oil/S_2 = *e*/*f*.

The above four points are related to one another by the fact that what-

ever the composition of the solvent mixture, the oil–solvent ratio in the complex represented by each, is always constant and equal to e/f.

This relationship is obvious by the plot of these points on the triangular

FIG. 8.

FIG. 9.

graph in Fig. 9. In this figure W represents as before pure wax, O' represents a mixture composed of oil and solvent S_1 whilst S' represents a mixture composed of oil and solvent S_2. The solvent oil-mixtures represented by the points O' and S' must be such that the oil/S_1 ratio and the

oil/S_2 ratio in each mixture is identical. The four points G, H, I, and J of Fig. 8 when plotted on this diagram give the curve GJ, which represents the equilibrium relationship for the system wax–oil–solvent S_1 and solvent S_2, where oil/S_1 ratio or oil/$(S_1 + S_2)$ ratio or oil/S_2 ratio is constant at e/f, whilst the ratio of S_1/S_2 is changing.

In a similar manner other curves, such as MN and YZ for different ratios of oil–solvent or oil–solvent mixture may be drawn.

This diagram may be used for the calculation of intermediate constant solvent–solvent ratio curves by interpolation. If, for example, the constant solvent–solvent ratio curve for the system wax–oil–solvent S_1–solvent S_2 when $S_1/S_2 = x/y$ is desired, then in Fig. 9 the point L, where $O'/S' = x/y$, is located and W joined to L. If $O'/S' = x/y$, then oil/S_1 ratio $= x$ and oil/S_2 ratio $= y$ and hence $S_1/S_2 = x/y$. The intersections of WL with the curves MN, QR, etc., in Fig. 9 then give the solubilities of wax in oil–double solvent $(S_1 + S_2)$ mixtures, where $S_1/S_2 = x/y$. The constant solvent–solvent ratio curve so determined will be incomplete due to the absence of the solubility of wax in an oil-free mixture of $S_1 + S_2$, where $S_1/S_2 = x/y$. This data, however, may be obtained and the curve completed by simple extrapolation to the wax–solvent side of the triangle.

In the preceding pages methods of representation for wax–oil–solvent–solvent system where both the solvents are miscible with the oil at the dewaxing temperature have been described. These methods of representation can, of course, be applied to the case where one of the solvents is partly miscible with the oil at the dewaxing temperature. An example of this type is the industrially important wax–oil–acetone–benzol system. Although in this system one of the solvents, acetone, is normally only partly miscible with the oil at operating temperatures, and hence the system does not truly come within the class being considered, nevertheless a wide range of acetone–benzole mixtures is completely miscible with most oils. Owing to the great technical interest attached to this system, equilibrium data for an oil–wax–acetone–benzole system have been included here. Fig. 10 represents by means of the prism type model the equilibrium between Burma wax (melting point 108° F.), Anglo-Iranian second cooled blue oil, acetone, and benzol at 50° F. The equilibrium data for the wax–oil–benzol system was obtained by the filtration method, that for the wax–acetone–benzol system was obtained by the cloud-point method. The data for the two liquid-phase regions of the diagram were not determined. Above the acetone–benzol ratio denoted by X on Fig. 10 the solvent, acetone, or acetone–benzol mixture is not completely miscible with the oil, and a second liquid phase appears. At any acetone–benzol ratio smaller than that represented by point X on the figure the quaternary system will, whatever its composition, always form one liquid phase—that is, it may form a single liquid phase only, or form a single liquid phase co-existing with a single solid phase. At any greater ratio the quaternary system can form two liquid phases either with or without a co-existing solid phase. Normally dewaxing is carried out at acetone–benzol ratios smaller than X, where the equilibrium has the same form as that encountered in oil-miscible double-solvent systems, and the curves AB and CD in Fig. 10 are constant solvent–solvent ratio curves for the system.

Double-solvent equilibrium data may be represented as described above

by the use of solid models. A regular tetrahedron or an equilateral triangular prism may be employed for this purpose. It is difficult to construct such models which will be exactly quantitative, and hence suitable projections of these models are normally employed. The most convenient graphical representation of isothermal equilibrium in a double-solvent system is the projection of the prism model on to its triangular base. This method of representation is easy to follow and simple to use for computation purposes. In addition, it can be employed to represent equilibrium in a

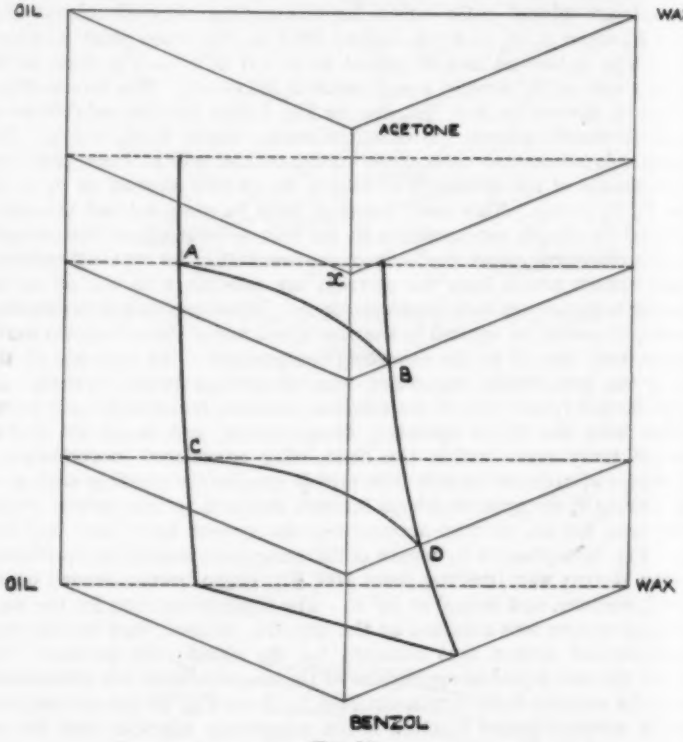


FIG. 10.

triple solvent system by maintaining suitable solvent–solvent ratios constant. The computation methods for single solvent systems already described [1] can of course be applied to the projection diagram on the triangular prism base.

COMPARISON OF CALCULATED AND EXPERIMENTAL DATA FOR A SYNTHETIC STOCK.

Small-scale dewaxing operations were carried out using synthetic stocks obtained by dissolving refined Burma wax, melting point 108° F.,

in Anglo-Iranian second cooled blue oil. The same apparatus and procedure as those previously described were followed. Dewaxing of these stocks using an acetone–benzol mixture, miscible with the oil at the operating temperature of 50° F., was carried out varying both the solvent–oil ratio and the acetone–benzol ratio. The results are given in Table I.

TABLE I.

Acetone–Benzole Mixture.

Run No.	Oil Stock Used.		Solvent/ Oil Ratio.	Solvent/ Solvent Ratio.	Dewaxing Temp. ° F.	Cake.			Dewaxed Oil.			
						Melting Point, ° F.	Per Cent Yield.		Pour Point, ° F.		Per Cent. Yield.	
	Per Cent. Wax.	Pour Point, ° F.					Actual.	Calc.	Actual.	Calc.	Actual.	Calc.
18	30·0	75·0	2·00	3 : 2	50	96·5	24·4	30·5	63	61	75·6	69·5
19	30·0	75·0	1·00	3 : 2	50	100·5	26·4	28·2	57	58	73·6	71·8
20	21·5	68·5	0·45	3 : 2	50	99·0	16·2	19·1	56	55	83·8	80·9
21	30·0	75·0	1·00	3 : 7	50	90·3	27·5	26·6	68	68	72·5	73·4
22	30·0	75·0	0·75	3 : 7	50	89·6	31·0	35·2	66	66	69·0	64·8
23	30·0	75·0	0·50	3 : 7	50	88·5	40·4	42·9	62	63	59·6	57·1
24	24·0	70·5	0·25	3 : 7	50	78·0†	57·7	51·1	58	58	45·3	48·9

In columns 2 and 3 the wax content and pour point of the oil stock used are given. The solvent–oil ratio, solvent–solvent ratio and dewaxing temperatures employed are detailed in columns 4, 5 and 6. In column 7 the melting point of the cake obtained experimentally is tabulated. The calculated yields of cake and dewaxed oil, and the pour point of the dewaxed oil, shown in columns 9, 11, and 13 respectively, were computed graphically, assuming the melting point of the cake was that shown in column 7. The actual yields and pour points are given in columns 8, 10 and 12.

TABLE II.

Amyl Alcohol–Methylethyl Ketone-Light Naphtha Mixture

Run No.	Oil Stock Used.		Solvent/ Oil Ratio.	Ratio of Amyl-Alcohol/Methyl-ethyl Ketone/ Naphtha in Solvent.	Dewaxing Temp., ° F.	Cake.			Dewaxed Oil.			
						Melting Point, ° F.	Per Cent. Yield.		Pour Point, ° F.		Per cent. Yield.	
	Per cent. Wax.	Pour Point, ° F.					Actual.	Calc.	Actual.	Calc.	Actual.	Calc.
25	22	69	2·0	7 : 2 : 1	50	95·5	19·8	22·8	54·0	54	80·2	77·2
26	22	69	1·5	7 : 2 : 1	50	95·5	21·7	23·6	52·0	53	78·3	76·4
27	22	69	1·0	7 : 2 : 1	50	90·5	27·7	31·0	51·5	51	72·3	69·0
28	22	69	1·0	7 : 2 : 2	50	90·5	25·8	27·9	55·0	55	74·2	72·1
29	22	69	1·0	7 : 2 : 4	50	90·8	23·5	26·6	56·0	56	76·5	73·4

The results shown in Table II were obtained when a synthetic stock consisting of refined Burma wax dissolved in Anglo-Iranian second cooled blue oil was dewaxed at 50° F. using a solvent mixture composed of the three solvents amyl alcohol, methyl ethyl ketone, and light naphtha (boiling point 100–120° C.).

The calculated results in both tables were computed from equilibrium

diagrams which were projections of the prism model. It will be seen from the tables that fair agreement between actual and calculated results has been obtained.

Discussion.

It has been shown in the present and two previous papers that in a system consisting of a commercial grade refined wax, low viscosity hydrocarbon oil free from asphalt and one, two, or more solvents, equilibrium may be represented by the usual phase-rule graphs and models. In order to make this possible the substances wax and hydrocarbon oil have been treated as if they were single components. For the particular materials employed this is justifiable, in so far as any mixture of such materials likely to result from the work could be easily analysed with reasonable accuracy in terms of wax and oil.

It has been shown also that the equilibrium diagrams evolved could be successfully employed for forecasting dewaxing operation results on a synthetic stock comprising refined wax and low-viscosity asphalt-free oil. The results obtained by such computations are quantitatively exact if the dewaxed oil and wax cake obtained are reported in terms of wax and oil content. Under these conditions the accuracy of the diagrams is governed entirely by the accuracy of the analytical methods employed. If, however, as has been done throughout, the dewaxed oil and wax cake are described in terms of pour point and melting point, the equilibrium diagrams no longer become exactly quantitative. Since, as has been pointed out in the first paper [7] and also by Kalichevsky,[6] who has given a good example of this, variation in wax composition with degree of dewaxing is not taken into account in the method employed, and consequently variation in the melting point of the wax with degree of dewaxing is ignored, and introduces a certain amount of error into all the computed data. It has been shown, however, that this error is small in the case of a synthetic stock where the total wax content is a commercial grade refined wax. Out of twenty-nine small-scale dewaxing runs, the maximum percentage error occurring in the calculated pour point of the dewaxed oil was −3·2 per cent., and the maximum percentage error in the calculated yield of the dewaxed oil was −8·1 per cent., whilst the average percentage errors were −0·1 per cent. and −2·1 per cent., respectively.

It can be concluded, therefore, that the methods are correct to within the limits of approximately ±5 per cent. for calculating yields and pour points of dewaxed oils on synthetic-type stocks consisting of refined wax blended with asphalt-free oil.

An important question in connection with this work is the possibility of applying these methods to forecasting results from commercial dewaxing operations. It should be emphasized here that the methods in their present form have never been claimed to be generally applicable to this purpose.

The methods evolved to date have been strictly confined to conditions where the wax was distinctly different from the oil, and from which it was possible to separate it quantitatively. In commercial practice wax cannot generally be considered as a substance of well-defined character, distinctly different and quantitatively separable from oil. Most of the commercial solvent dewaxing processes are concerned with the removal of wax from

non-pressable fractions. This so-called "wax" is a substance of ill-defined character and of intermediate properties capable of classifying it as either oil or wax. This fact alone presents very considerable difficulties to the successful application of the methods to commercial practice.

The heavier non-pressable fractions employed as stocks in commercial dewaxing frequently contain resinous and asphaltic substances, which may separate out as a second liquid phase on the addition of solvent. The methods described are not designed to meet such conditions, but could probably be modified to apply to such cases. Even so, the ill-defined character of the "wax" present is still a difficulty.

The presence of pour-point depressants is also an additional complication.

There must exist, of course, certain cases where the methods are applicable. It is emphasized here, however, that the methods, in their present form, cannot generally be used for accurate or reliable computations in commercial dewaxing operations.

The aim in carrying out this research has been the investigation of dewaxing principles on a quantitative fundamental basis. Owing to the complicated and ill-defined nature of the raw materials, wax and oil, the work has necessarily been confined within strict limits with regard to the properties of these materials. While in the long run, when dealing with a complex material like petroleum, recourse to actual experimental data will probably always be necessary, it is obvious that if a quantitative fundamental basis for the explanation of process results and for the consideration of process variables exists, such experimentation may be reduced to a minimum, and considerable economy will eventually result.

This economy will be obviously greatest when the general effect of process variables, the comparative efficiency of different processes and different operating methods can be derived from quantitative fundamental principles. In many cases where such comparative data are the only requirement, computation alone on a suitable fundamental basis may be sufficient. In the majority of such cases computation combined with a minimum of laboratory experiments may be employed. It is obvious from these considerations that the investigation of quantitative principles will eventually prove of practical benefit. Some of the possible applications of the above methods will be described in later publications.

The Department of Oil Engineering and Refining,
The University of Birmingham.

References.

[1] Ba Thi, Strang, Hunter, and Nash, *J.I.P.T.*, 1937, **23**, 226.
[2] Ba Thi, Hunter, and Nash, *ibid.*, 1937, **23**, 707.
[3] Verver, *ibid.*, 1937, **23**, 754.
[4] Auld, *ibid.*, 1937, **23**, 753.
[5] Thompson, *ibid.*, 1937, **23**, 757.
[6] Kalichevsky and Lee, *ibid.*, 1938, **24**, 59.
[7] Ba Thi, Strang, Hunter, and Nash, *ibid.*, 1937, **23**, 234.

ANNUAL REPORT.

Trinidad Branch.

The following is the Report of the Committee on the Working of the Branch during the Session 1936–1937.

Three meetings were held during the session at which the following papers were read :—

2nd December, 1936—*Ninth Annual General Meeting.*

"Forestry in Relation to the Petroleum Industry." By Mr. R. L. Brooks, Dipl.For.(Edin.), Conservator of Forests, Trinidad and Tobago.

24th February, 1937—*Forty-ninth General Meeting.*

"Marine Drilling." By Mr. A. J. Ruthven-Murray, M.A., B.Sc. (Branch Chairman).

31st March, 1937—*Fiftieth General Meeting.*

"The Chemical Treatment of Trinidad Drilling Fluid." By Mr. I. McCallum, B.Sc. (Assoc. Member).

The average attendance of members and guests at meetings was 31.

Mr. A. J. Ruthven-Murray was elected Chairman, and Mr. H. W. Reid was re-elected Honorary Secretary and Treasurer for the Session.

The Committee wishes to record its appreciation of the services to the Branch of Commander H. V. Lavington, R.N., who resigned the Chairmanship at the end of last session.

In March 1937 Lord Cadman visited the Colony, and members of the Branch were entertained by him at a dinner given in Port-of-Spain, at which the principal guest was His Excellency the Governor, Sir Murchison Fletcher, K.C.M.G., C.B.E. Sixty-three guests were present. In view of this, it was decided that the usual annual dinner would not be held during the Session.

At the end of the year there were 68 members on the roll of the Branch.

The Committee wishes to record the thanks of the Branch to Mr. W. G. Dale and Mr. D. M. Walsh for their services as Auditors, and to Mr. W. N. Foster who acted as Honorary Secretary during the latter's absence on leave.

A. J. Ruthven-Murray,
Chairman.

H. W. Reid,
Hon. Secretary and Treasurer.

1st December, 1937.

THE INSTITUTE OF PETROLEUM

TRINIDAD BRANCH

ACCOUNTS FOR THE YEAR ENDED 31ST OCTOBER, 1937.

REVENUE ACCOUNT.

Stenographer's Remuneration	$42.00	Quarterly grants from London	$192.00
Postage, Printing, Etc.	36.07	Enrolment fees	2.00
Loss on 6th Annual Dinner	46.48		
Surplus for the year	69.45		
	$194.00		$194.00

BALANCE SHEET.

Surplus Brought Forward		$207.96	Balance at Bank		$383.70
Surplus for the year		69.45	Cash in hand		10.15
Sundry Creditors :—					
Benevolent Fund	$78.00				
Ape (T'dad) Oilfields, Ltd.	3.16				
H. W. Reid	35.28				
		116.44			
		$393.85			$393.85

A. J. RUTHVEN-MURRAY,
Chairman.
H. W. REID,
Hon. Secretary and Treasurer.

D. M. WALSH, W. G. DALE } *Auditors.*

OBITUARY.

ARTHUR ALAN ASHWORTH.

Mr. Arthur Alan Ashworth, M.A., A.M.I.C.E., M.Inst.P.T., who died in London on 27th June, in his 71st year, was educated at St. Paul's School and Christ's College, Cambridge, where he took an honours degree in Mathematics. His early engineering training 1890–1893 was with Michael Longridge, M.I.C.E.—where he was engaged on research work in connection with heat transmission of metals—and later with the Manchester Ship Canal. In 1893 he was Assistant Engineer on the Colombian Railways Surveys, in consequence of which he suffered severely from malaria. On his return home he accepted a post as engineer on the North-Eastern Railway, and subsequently occupied a similar post on the South African Railways. For some time he was engaged by the Whessoe Foundry Co., Ltd., where he obtained a sound knowledge of tank design.

Mr. Ashworth's first connection with the oil industry was in Russia in 1910, when, after an engagement on the Baku Water Supply, he worked on the Maikop pipe-line to the Black Sea.

From 1912 to 1920 he was General Manager of the Kansas Oil & Refining Co., Ltd., and the Alluwe Oil Co. of Kansas-Oklahoma, and established a high reputation in those fields by his advanced views on oil-refining and field development.

In 1920 Mr. Ashworth became a partner in the firm of A. Beeby Thompson & Partners, and in that capacity specialised in oil-refinery questions. Between 1920 and 1938 he was responsible for refinery designs and reconstructions in a number of countries, and was specially interested in high-vacuum and pipe-still work. During the same period he was largely responsible for the design and layout of water-work schemes, submarine and land oil-pipe lines, oilfield development programmes, and oil-storage installations. He was, however, most at home on research work in the laboratory, and he was never happier than when engaged on elucidating oil problems.

Mr. Ashworth became a member of the Institute of Petroleum in 1924. He was later co-opted on various Technical Sub-Committees of the Chemical Standardization Committee, and was the contributor of several articles and letters to the Institute's *Journal*. In 1933 Ernest Benn & Co. published a work under his authorship entitled "Analysis of Oil for the Production of Lubricants."

Mr. Ashworth leaves a large circle of friends, whose sympathy will be extended to his wife, son and daughters in their bereavement.

A. B. T.

[*Reprinted from the Journal of the Institution of Petroleum Technologists, Vol. 24, No. 179, pp. 471–495, Sept., 1938.*]

THE POLYMERIZATION OF ETHYLENE WITH COMPOUNDS OF ALUMINIUM AS CATALYST.

By F. C. HALL, Ph.D., A.I.C. (Associate Member), and A. W. NASH, M.Sc., F.C.S., M.I.Mech.E., M.I.Chem.E. (Member).

SUMMARY.

The catalytic polymerization reactions of ethylene are reviewed with particular reference to that induced by aluminium chloride. The effect of metallic aluminium on this latter reaction has been investigated at varying temperatures and is described in detail. The products of reaction include organo-metallic ethyl derivatives of aluminium and polymerized hydrocarbon oils of high boiling point. The residual and distillate lubricating-oil fractions therefrom have relatively high viscosity indices in contrast to those from the polymerization of ethylene with aluminium chloride alone, the optimum values being obtained for oils from the reaction at 200°.

It is shown that the cracking action of aluminium chloride on hydrocarbon oils may be completely inhibited by the presence of metallic aluminium or magnesium, zinc having a less pronounced effect.

At temperatures above 200° C. the polymerization reaction is further complicated by the catalytic activity of the aluminium ethyl derivatives. Under suitable conditions high yields of butene-L, hexenes and octenes can be obtained by direct polymerization of ethylene, using either aluminium diethyl chloride or the simple aluminium chloride–aluminium catalyst. The reaction is shown to be in accordance with the mechanism proposed by Taylor and Jones for the polymerization of ethylene by free alkyl radicles, and it is suggested that these radicles are derived from the incipient thermal decomposition of the aluminium ethyl compounds.

THE direct polymerization of ethylene under pressure, in the absence of catalysts, is found to commence at approximately 325° C. and is quite rapid at 375–400° C.[1, 2, 3, 26] Under certain conditions the reaction may become explosive with exothermic decomposition into carbon and hydrogen.[4] The liquid products normally obtained are relatively low boiling, highly unsaturated, and contain olefine, paraffin and naphthene hydrocarbons.

In the presence of aluminium chloride the polymerization is effected at much lower temperatures, although little reaction is found at ordinary pressure. The reaction under high pressure was investigated in detail by Stanley;[2, 3] his conclusions can be briefly summarized as follows: At low temperatures (10–15° C.) a saturated "free oil," containing chiefly naphthenes of which only 17 per cent. distilled below 100° C. at 10 mm., together with an insoluble pasty "double compound," is formed. The double compound contains aluminium chloride in combination with cyclic unsaturated hydrocarbons which can be liberated as a "combined oil" by decomposition with water; it remains substantially constant in amount during the production of considerable quantities of the "free oil." At higher temperatures (100–150° C.) the reaction proceeds more rapidly, with formation of an increasing amount of low-boiling paraffin hydrocarbons. The heavier fractions of the free oil become more aromatic in character,

with high carbon : hydrogen ratio, whilst the double compound is more carbonaceous in appearance and deteriorates more rapidly in catalytic activity.

In Stanley's view the reaction proceeded through the intermediate formation of higher olefines which isomerized to the corresponding naphthenes. At higher temperatures the latter suffered an increasing degree of decomposition (cracking) to give light paraffin hydrocarbons and heavy oils of lower hydrogen content. He suggested that the actual polymerization might proceed through the intermediate addition of hydrogen chloride to the olefine molecule by a form of Friedel–Crafts reaction. Support for a reaction mechanism involving hydrogen chloride as an intermediate reactant is afforded by the observation of Ipatieff and Grosse,[5] that the reaction is inhibited in the absence of traces of hydrogen chloride. Waterman, Leendertse and ter Poorten [6] have found hydrogen chloride to have a pronounced accelerating action on the polymerization of *cyclo*hexene, whilst a comparable action has been observed in other condensation, isomerization and decomposition reactions, involving aluminium chloride.[7, 8, 9, 10] A reaction mechanism, on electronic considerations, based on the distortion or polarization of the valency electrons of the olefine molecule through association with the aluminium chloride to form a co-ordination complex, has been put forward by Hunter and Yohe.[11] A further attempt to represent upon an electronic basis, the catalytic activity of aluminium chloride, particularly in reactions of the Friedel–Crafts type, has been made by Dougherty [12] on the supposition that a form of ionized complex is produced, capable of reactions analogous to those of inorganic ions in solution.

It is probable that the polymerization initially proceeds through the formation of the simple dimer of ethylene, particularly in that this olefine (butene-1) can be isolated when using very short reaction periods.[13] Under the usual conditions, however, the free hydrocarbon polymers are substantially saturated. Ipatieff [14] suggests that the low-boiling paraffins formed in the high-temperature polymerization are chiefly derived, not from cracking reactions induced by the aluminium chloride, but from the hydrogenation of low-molecular-weight olefine polymers, the hydrogen being derived from the dehydrogenation of naphthenes to aromatic hydrocarbons.

The properties of the high-boiling fractions obtained from the polymerization of ethylene with aluminium chloride, and their value as lubricating oils, were investigated by Stanley,[2] who showed that the viscosity/temperature characteristics of even the low-temperature polymers were poorer than those of normal petroleum lubricants. The high-temperature polymers had exceptionally low viscosity indices (of the order of −200), due probably, as suggested by Petrov and Antzuz,[15] to the aromatic constituents present. Examination of these polymers by the Waterman method indicates that they have an essentially simple cyclic structure [16] (not polycyclic), the low-temperature polymers being largely *iso*-paraffinic, with highly branched side chains.[17]

Atkinson and Storch [18] obtained lubricating-oil fractions from ethylene by first polymerizing to liquid unsaturateds through pyrolysis, followed by further polymerization with aluminium chloride. The resultant oils had

viscosity indices of 50–100. A similar procedure has been used by the Fuel Research Board.[19]

The value of the low-boiling polymers for motor fuel was investigated by Bowen and Nash,[20] who found the fraction distilling below 190° C. from the polymerization reaction at 190° C., to have an octane rating of 73. In general, however, attention has been directed towards thermal polymerization, or catalytic polymerization with phosphoric acid catalysts, for the conversion of ethylene into motor fuels. The relatively short life of the aluminium chloride catalyst when used in high-temperature polymerization is a serious drawback.

Various modifications of the normal aluminium chloride catalyst have been suggested. Howes [21] proposed to use aluminium chloride with the addition of powdered nickel or aluminium and also to support the catalyst on a kieselguhr carrier. The catalyst was claimed to reduce the yield of combined oil. The double compound of aluminium chloride obtained in polymerization reactions is itself an active catalyst,[22] whilst double compounds with polar organic compounds, such as nitrobenzene, with organic acids (giving the "ansolvo acids"), and with inert metallic halides such as sodium chloride, have geen suggested as polymerization catalysts.[23] Other inorganic halides have been used for olefine polymerization; of these, boron trifluoride alone has so far proved of importance. Using this material, Otto [24] found that ethylene polymerized at room temperature, the reaction being accelerated by traces of water, halogen acids or halogen compounds, and by the presence of finely divided metals, especially nickel.[25] Ipatieff [14] has recently stated that the polymerization of ethylene by boron trifluoride will not proceed at all in the absence of metallic nickel. The higher-boiling fractions were stated by Otto to be excellent lubricating oils, having reasonably high viscosity indices (of the order of 50). According to Ipatieff, the low-boiling fractions from the reaction at room temperature are predominantly mono-olefines, and high yields of butene have been claimed by the use of a short reaction time.[13] Boron trifluoride, whilst more difficult to manipulate than aluminium chloride, has the advantage of being nearly completely recoverable from the reaction products by simple heating.

The experimental work described in this paper was commenced with the object of finding some means of controlling the catalytic action of aluminium chloride in such a manner that lubricating oils of reasonably good viscosity indices could be obtained from the polymerization of ethylene.

In the preliminary work an attempt was made to secure direct hydrogenation of the intermediate "nascent" polymerization product from the action of aluminium chloride on ethylene at relatively elevated temperatures. A mixture of ethylene and hydrogen at 80 atmospheres was heated to 150° C. with 30 gms. of aluminium chloride and 10 gms. of aluminium turnings. The product after two hours' polymerization was found to differ very markedly from that obtained through the action of aluminium chloride alone. It was a reddish-brown liquid evolving white fumes in the air, and reacting violently with water. Experiments showed that this reaction was due to the presence of the aluminium metal, the hydrogen having no appreciable effect. It was found, in addition, that the hydro-

carbon polymers of higher molecular weight formed in this reaction had viscosity indices very much higher than those of the normal aluminium chloride–ethylene polymers. The work described in this paper deals with the various aspects of this reaction and of associated phenomena.

Experimental.

Part I.—The Polymerization of Ethylene at 100–200° C. by Aluminium Chloride in the Presence of Aluminium Metal.

The ethylene used throughout this work was that supplied by the British Oxygen Company. The following analysis was obtained on the Bone-Wheeler apparatus:

	%
Higher olefines . . .	0·4
Ethylene	98·0
Paraffins	0·8
Nitrogen	0·8

The autoclaves used were 2-litre rotary Bergius-type steel bombs, previously used by Stanley for his polymerization work. The autoclaves

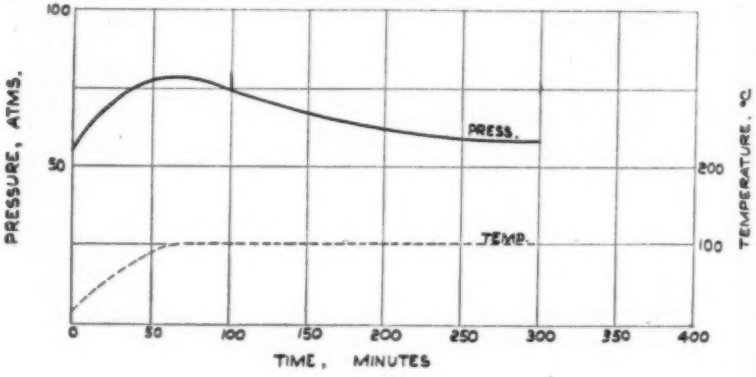


Fig. 1.

Ethylene polymerization at 100° C.

were heated directly by gas, and the temperature measured by recording thermometers. No liners were used

The aluminium chloride used was the anhydrous sublimed product supplied by British Drug Houses. This product was found to be practically as catalytically active as the material re-sublimed immediately before use, and was of uniform activity.

The formation of a product reactive towards air and water was found to take place most readily at temperatures of the order of 100–200° C., in the presence of an excess of metallic aluminium. If sufficient ethylene was initially present, the reaction eventually ceased with an excess of ethylene remaining in the autoclave. The temperature–time–pressure curves illustrating this for experiments at 100° and 200° are given in Figs. 1 and 2.

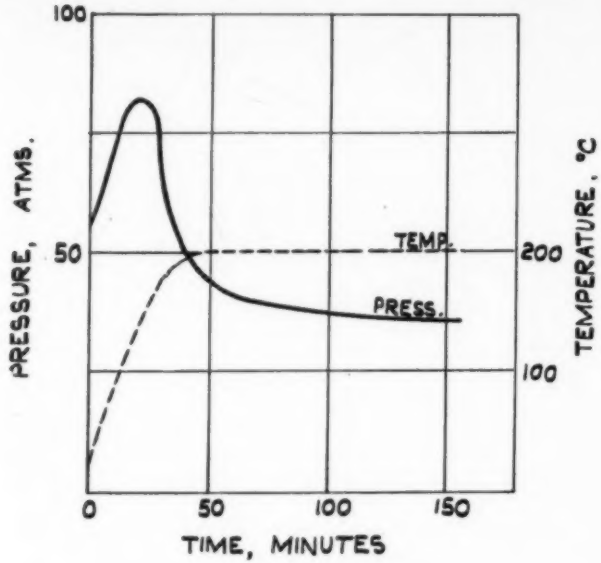


FIG. 2.
ETHYLENE POLYMERIZATION AT 200° C.

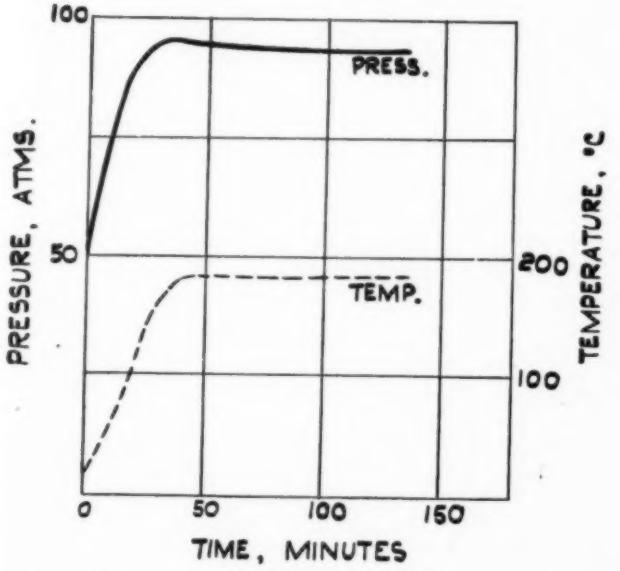


FIG. 3.
ETHYLENE POLYMERIZATION AT 180° C. [ALUMINIUM POWDER].

At temperatures over 250° the absorption of ethylene appeared to proceed indefinitely, giving a product of much lower reactivity. No evidence for such a reaction was observed to occur at room temperature (10–15°) over long periods, but otherwise the reaction at temperatures below 100° was not investigated.

The use of very finely divided aluminium powder (such as used in paint manufacture) accelerated the reaction, the ethylene absorption rapidly ceasing and leaving a high residual pressure (Fig. 3). The product of this polymerization was found to be especially reactive. Certain samples of aluminium turnings showed lower activity, necessitating refilling the autoclave with ethylene before the absorption ceased. The use of freshly sublimed aluminium chloride resulted in no appreciable alteration of the reaction, but no experiments were carried out in which residual traces of hydrogen chloride were expressly excluded.

Characteristics of the Product.—The residual gas in the autoclave was chiefly ethylene, with traces of paraffins, and contained no higher olefines.

The liquid was generally homogeneous, mixed with a sludge of unreacted aluminium and traces of oxidation products. For investigation it was transferred from the autoclave to nitrogen-filled tubes, centrifuged, and the clear liquid stored under an atmosphere of nitrogen or hydrogen. Transference of the liquid was carried out by nitrogen or hydrogen displacement to avoid oxidation.

Properties.—The reactivity of the liquid towards air and water has been referred to. The product from polymerization at 100–200°, especially when using finely-divided aluminium powder, became hot on exposure to the air, evolving dense white fumes which were found to contain aluminium and chlorine. On decomposition with water, dilute acid or alkali, considerable quantities of ethane were evolved. The aqueous solution contained aluminium and chlorine ions, and a yellow oil of hydrocarbon nature separated as a second liquid phase. The liquid product reacted violently with hydroxy-compounds (alcohols, phenols) and with certain chloro-compounds (amylene dichloride, benzyl chloride, but *not* chlorobenzene).

Table I illustrates the variation in aluminium and chlorine content with change in experimental conditions, the analytical figures being determined

TABLE I.

Catalyst.	Reaction Temp., ° C.	Reaction Time, hrs.	Analysis of Product.		
			Al, %.	Cl, %.	Atomic Ratio Al : Cl.
30-gm. $AlCl_3$: 10-gm. Al (Al granules) . . .	100	3·5	8·6	13·1	1 : 1·17
30-gm. $AlCl_3$: 10-gm. Al (Al granules) . . .	180	2	6·95	10·8	1 : 1·18
30-gm. $AlCl_3$: 10-gm. Al (Al granules) . . .	300	1	4·1	7·1	1 : 1·32
30-gm. $AlCl_3$: 10-gm. Al (Al powder)	200	1·5	12·1	22·0	1 : 1·38

by hydrolysis and subsequent estimation of aluminium and chlorine in the aqueous extract.

An investigation of the nature of the product was made, and has been reported in detail in a previous communication.[27] The material investigated was that obtained from the polymerization of ethylene at 150° C. by aluminium chloride and finely divided aluminium powder. It was concluded that the liquid polymerization product was a solution of aluminium ethyl chlorides in a viscous hydrocarbon oil, the organo-metallic compounds comprising between 40 and 50 per cent. of the crude product. The aluminium ethyl chlorides were separated as a mixed fraction by fractional distillation under vacuum, and were found to be colourless, spontaneously inflammable liquids of extremely reactive characteristics. By extraction with sodium chloride a fraction of b.pt. 85–86·5°/9·5 mm. (214–215°/760 mm.) was finally isolated, the composition of which approximated closely to that of aluminium diethyl chloride, $Al(C_2H_5)_2Cl$.

Hydrocarbon Oils from the Polymerization of Ethylene by Aluminium Chloride and Metallic Aluminium.

Reference has been made to the hydrocarbon polymers which occur in solution with the aluminium ethyl chlorides. Upon decomposition of the crude polymerization product (preferably in an inert solvent, such as petroleum ether) with water, dilute acid or alkali, these hydrocarbon polymers separate as an oil layer. At polymerization temperatures below 200–250° this oil contains a negligible proportion of components boiling below 100°, and may be recovered from its solution in light petroleum ether by distillation. The properties of a series of lubricating oil fractions have been briefly described by the authors elsewhere.[28] The yields and viscosities of the separated oil from polymerization at 200° using different grades of aluminium metal are illustrated below :

TABLE II.

Catalyst : 30 gms. aluminium chloride + 10 gms. aluminium.

Aluminium Used.	Wt. of Ethylene Absorbed, gms.	Oil from Hydrolysis Distilling above 100°/760 mm.	
		Yield, gms.	Viscosity, Centistokes at 100° F.
Needle filings . . .	223	152	44
Fine granules . . .	174	130	57
Fine powder . . .	68	34	2430

The oils produced are essentially hydrocarbons (confirmed by microcombustion analyses), but it is believed that traces of oxygen-containing compounds are also present, particularly if the initial polymerization product is exposed to any degree of atmospheric oxidation. The oils obtained are sharply differentiated from the corresponding aluminium chloride polymers by the absence of low-boiling hydrocarbons, and by the viscosity indices of the heavier fractions.

The distillation figures for a series of oils from the polymerization of ethylene by aluminium chloride and aluminium granules (30 gms. : 10 gms.)

at 100°, 200° and 300° are given in Table III, two oils from the direct polymerization of ethylene with aluminium chloride being included for comparison. The marked reduction in low-boiling constituents of the oil from the polymerization at 200° compared with that from polymerization with aluminium chloride alone at a lower temperature (150°) is very evident. The polymerization at 300° is discussed later in this paper.

The properties of a series of distillate lubricating-oil fractions taken from these products are summarized in Table IV.

TABLE III.

Distillation Characteristics of Ethylene Polymerized Oils.

Catalyst.	30-gm. $AlCl_3$: 10-gm. Al granules.			$AlCl_3$.	
Reaction temperature	100°	200°	300°	20°	150°
Yield of oil, gms.	110	130	660	—	—
Per cent. yield of oil from total autoclave product	61	57	—	—	—
Viscosity of oil at 100° F. centistokes	101	57	—	—	—
Distillation (% wt.):					
0–100°	—	—	7·2	—	22·1
100–200°	6·8	8·8	21·5	—	27·9
200°/760 mm.–150°/10 mm.	13·9	14·9	25·8	34·5 *	14·3
150–200°/10 mm.	13·3	11·5	15·0	11·6	15·9
200–250°/10 mm.	11·8	10·7	11·1	14·0	11·0
Residue above 250°/10 mm.	54·2	54·1	19·5	39·8	8·8

* Total fraction below 150°/10 mm.

TABLE IV.

	Oil from Polymerization with Aluminium–Aluminium Chloride Catalyst at:						Oil from Polymerization with Aluminium Chloride Catalyst at:	
	100° C.		200° C.		300° C.			
	Light.*	Heavy.†	Light.	Heavy.	Light.	Heavy.	15° C.	150° C.
Viscosity in centistokes at 100° F.	50·2	247	34·7	172·5	28·9	217	112	200
Viscosity in centistokes at 210° F.	5·76	13·8	4·86	12·0	4·32	13·2	7·7	7·8
Viscosity index	35	30	45	50	35	40	−30	−230
Sp. gr., 60/60° F.	0·861	0·875	0·871	0·885	0·867	0·890	0·836	0·921
Viscosity gravity constant	0·798	0·788	0·818	0·808	0·816	0·811	0·750	0·857
Pour point, ° F.	—	below 10	—	below 10	—	below 10	—	—

* Light oil: fraction 200°/10 mm.–250°/10 mm.
† Heavy oil: fraction 250°/10 mm.–280°/2 mm.

The viscosity indices of the fractions are very much higher than those of fractions from the polymerization of ethylene with aluminium chloride alone, and show an optimum value for the reaction at 200° The viscosity gravity constants of these fractions, as with other synthetic polymerized oils, are of little significance, being consistently low. The fraction from aluminium chloride polymerization at 15° is of interest in this connection, possessing the remarkably low value of 0·75 with a viscosity index of −30.

Oxidation tests on these fractions showed a lower degree of stability than for corresponding petroleum fractions. The high viscosity index oils from the polymerization at 200° were particularly poor, giving a deposit of a light-coloured flocculent sludge upon oxidation, with increase in viscosity and carbon residue

Residual Fractions.

The properties of the residual fractions above 200°/10 mm. for a 30-gm $AlCl_3$: 10-gm. Al granules catalyst, are summarized in Table V.

TABLE V.

Reaction Temp., ° C.	Viscosity of Oil in Centistokes.		Viscosity Index.	Sp. Gr., 60° F.
	100° F.	200° F.		
100	5600	108	20	0·907
190	1610	62	67	0·902
300	3300	77	30	0·921

As with the distillate fractions, the optimum viscosity index is given at a polymerization temperature of approximately 200°. The effect of solvent treatment with aniline and nitrobenzene on the oil from the reaction at 200° is shown below.

TABLE VI.

	Yield, %.	Viscosity in Centistokes at:		Viscosity Index.	Sp. Gr., 60° F.	V.G.C.
		100° F.	200° F.			
Original fraction .	100	1610	62	67	0·902	0·794
Aniline raffinate .	73	2140	78	75	0·896	0·777
Nitrobenzene raffinate . .	65	2240	81	75	—	—

The increase in viscosity of the fraction obtained by solvent extraction is of interest, indicating the presence of high-molecular-weight hydrocarbons of relatively uniform chemical character. The original fraction showed comparatively low stability towards oxidation, yielding a light-coloured flocculent sludge, similar to that from the distillate oils. The aniline raffinate had considerably improved stability. It was observed that exposure of the original polymerization product (from the autoclave) to atmospheric oxidation, with subsequent hydrolysis and recovery of the oil, gave a product more susceptible to oxidation. It is possible, therefore, that the instability of these synthetic oil fractions is due to traces of unstable oxygenated compounds.

The effect of blending the viscous residual fractions in amounts up to 30 per cent. with petroleum base stocks was studied. The viscosity index of the base stock was in no case raised more than 8 units with a 30 per cent. blend, in contrast to the exceptionally high-blending viscosity indices of certain *iso*butylene polymers reported in the literature. The viscosity

indices of the residual fractions, determined from their blending value, appeared to be of the same order as those of the corresponding lighter fractions.

Reaction of Metallic Aluminium with Aluminium Chloride Double Compound.

Under the existing experimental conditions a considerable degree of ethylene ploymerization takes place before the normal reaction temperature is attained, as may be seen from the pressure-time-temperature graphs given. It is probable that this results in the intermediate formation of the aluminium chloride double compound, normally found in the absence of free aluminium. This double compound, like free aluminium chloride, is capable of reacting directly with metallic aluminium and ethylene, as was demonstrated by the following experiment. Ethylene was polymerized at 100° for 3 hrs. using 30 gms. of aluminium chloride as catalyst. After removal of the "free oil" formed, 15 gms. of aluminium granules were added to the residual viscous aluminium chloride double compound, and the autoclave heated to 180° for 2 hrs. No trace of any reaction was observed, except for the formation of a few grams of free oil and slight "carbonization" of the double compound. Upon introduction of ethylene to 55 atm. and again heating to 180°, the normal type of absorption was observed, with formation of a reactive liquid product, and with a complete absence of any insoluble aluminium chloride double compound.

Suppression of the Cracking Action of Aluminium Chloride by Metallic Aluminium.

The absence of low-boiling hydrocarbons in the polymerization of ethylene by aluminium chloride with metallic aluminium at temperatures of 100–200° C., and the small amount of gaseous paraffins formed in comparison with similar experiments using aluminium chloride alone, indicate that the normal cracking action of aluminium chloride at such temperatures is not in evidence. To investigate this, two experiments were carried out, using the 2-litre steel autoclave, in which a kerosine was subjected to the action of aluminium chloride at 200°, alone and with the addition of aluminium metal. 200 gms. of kerosine were used (sp. gr. of kerosine 0·808, aniline point 67° C.) with a reaction time of 2 hrs. at 200° C.

TABLE VII.

Catalytic Cracking of Kerosine.

Expt.	Catalyst.	Final Pressure Atm. at 200°.	Product Recovered.		
			Liquid, gms.	Solid, gms.	Type of Solid.
1	20-gm. $AlCl_3$	16	163	47	Pitch-like, hard product.
2	20-gm. $AlCl_3$ + 6·7-gm. Al granules	3	183	27	Soft, porous sludge.

Distillation curves for the initial kerosine and cracked products are given in Fig. 4, and show that the addition of the metallic aluminium has nearly completely suppressed the cracking reaction.

Further experimental work, using a small steel bomb, oil-bath heated, indicated that this effect was exhibited by magnesium and, to a less degree, by zinc. Table VIII summarizes the data obtained for a series of experiments at 200°, with a 2-hr. reaction time, using 150 gms. of kerosine, 15 gms. of aluminium chloride, and molar additions of various powdered metals. The " per cent. cracking " is derived from the percentage of the cracked liquid product distilling below the initial boiling point of the untreated kerosine. Included in the table is a column giving the heat of reaction of the metal and hydrogen chloride.

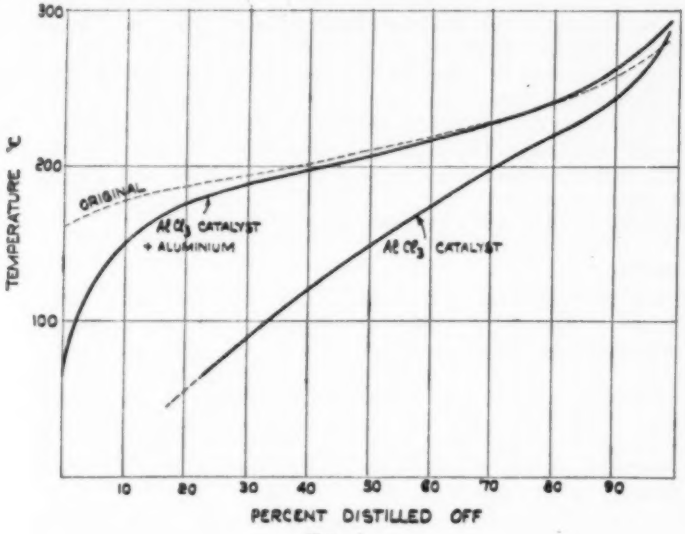


FIG. 4.

DISTILLATION OF CRACKED KEROSINES.

TABLE VIII.

Catalytic Cracking of Kerosine by Aluminium Chloride with Added Metals.

Metal Present.	Wt., gms.	Per cent. Cracking.	Heat of Reaction of Metal and Hydrogen Chloride, kg. cal./gm. mol.
None . . .	—	20	—
Aluminium . .	3·0	5	100·7
Magnesium . .	2·7	5	109·1
Zinc . . .	7·35	10	55·5
Copper . . .	7·15	17	10·5

According to Candea,[29] the presence of copper increases the cracking effect of aluminium chloride (in contrast to the data given here), whilst the addition of alkali chlorides has been stated to suppress cracking.[30] Apart from these instances, the effect of other substances on aluminium chloride in cracking reactions does not appear to have been investigated.

Ipatieff [10] and others have shown that the action of aluminium chloride on hydrocarbon reactions is dependent to a very great degree on the presence of free hydrogen chloride. It would therefore be anticipated that the addition of a substance altering the concentration or activity of hydrogen chloride would materially affect reactions involving aluminium chloride. In the examples studied, it is of interest to observe that the metals found to suppress cracking are those having a marked reactivity towards hydrogen chloride.

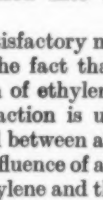
From these experiments it is apparent that in the polymerization of ethylene by aluminium chloride with metallic aluminium, the absence of low-molecular-weight paraffin hydrocarbons *formed by the cracking action of aluminium chloride* is to be expected.

A certain amount of polymerization work has been carried out using metals other than aluminium. Zinc, for example, reduced the extent of the normal aluminium chloride reaction, without materially altering the products. Magnesium was found to suppress polymerization very markedly at 200°, with formation of a saturated hydrocarbon oil, and scarcely any of the usual "double compound." In neither case were any soluble metallic derivatives detected in the hydrocarbon polymers.

Discussion.

In the experimental work described it is evident that in the reaction of ethylene with aluminium chloride and metallic aluminium at temperatures of 100–200°, the ethylene is polymerized to hydrocarbons of high molecular weight. At the same time, the aluminium chloride is itself transformed into ethyl derivatives, which dissolve in the hydrocarbon polymers and which, under the experimental conditions, are catalytically inert towards ethylene polymerization. When the aluminium chloride has been completely transformed into aluminium ethyl chlorides the polymerization ceases.

It is difficult to attribute a satisfactory mechanism to the reaction taking place, particularly in view of the fact that none is yet available for the relatively simple polymerization of ethylene by aluminium chlorine alone. The first stage in the basic reaction is undoubtedly the formation of a complex intermediate compound between aluminium chloride and ethylene. From the strong co-ordinating influence of aluminium chloride, it is probable that the linkage between the ethylene and the aluminium atom is not widely different from that existing between aluminium and the chlorine atoms. The complex could be represented by the structure advanced by Hunter and Yohe: [11]



In the normal aluminium chloride reaction the polarization of the terminal carbon atom would be expected to lead to polymerization by chain formation. In the presence of free aluminium it may be postulated that the terminal carbon atom is hydrogenated with formation of an ethyl grouping, attached by a covalent linkage to the aluminium atom. One of the

chlorine atoms can then split off in the presence of an acceptor such as the free aluminium, to re-form aluminium chloride. This hypothesis admittedly gives no explanation of the failure to obtain ethyl derivatives when magnesium or zinc is substituted for the aluminium metal.

Other reaction mechanisms can be devised, based, for example, on the initial formation of an unstable sub-chloride of aluminium, or on the intermediate reaction of ethyl chloride, but, in the absence of more specific experimental or theoretical justification, they must likewise be regarded as purely hypothetical. That a hydrogenation reaction takes place is evident; this in turn must be preceded by a dehydrogenation reaction in order that hydrogen be available. In this connection it is of interest that the reaction under consideration occurs at temperatures where, in the absence of free aluminium, quantities of low-boiling paraffins are formed. The reaction giving rise to low-boiling paraffins has been attributed by Ipatieff [14] to intermolecular hydrogenation. Assuming the validity of this, the absence of any appreciable quantities of low-boiling paraffins indicates that this intermolecular hydrogenation reaction has been suppressed in favour of the production of the aluminium alkyl chlorides.

The chemical and physical characteristics of the hydrocarbon polymers have not been sufficiently investigated for any very definite conclusions to be reached as to their chemical structure. They are essentially saturated, with a somewhat higher carbon : hydrogen ratio than the oils from the low-temperature aluminium chloride polymerization, and their high viscosity indices point to a type of structure containing a much higher proportion of long carbon chains. The products from the reaction at 100° approach more closely those from the aluminium chloride polymerization, having lower viscosity indices and specific gravities. It is probable that the presence of metallic aluminium, or of the aluminium ethyl chlorides, modifies the catalytic action of the aluminium chloride to the extent that polymers of greater chain length are initially formed, with subsequent cyclization and isomerization to saturated hydrocarbons of less highly branched structure. The hydrocarbons formed may, in addition, contain small amounts of unsaturated hydrocarbons derived from decomposition of the aluminium chloride-complex (" double compound "), which would be formed to some extent at the commencement of the reaction, particularly during the initial heating period. Further reaction of the " double compound " with aluminium and ethylene to form the stable aluminium ethyl chlorides would be expected to liberate the unsaturated hydrocarbons.

Part II.—Polymerization of Ethylene at Higher Temperatures.

Polymerization with Aluminium Chloride–Aluminium Catalysts.

The polymerization of ethylene at 300° with a 30-gm. $AlCl_3$: 10-gm. Al catalyst has been referred to. It was found that at this temperature the polymerization activity did not diminish to any great extent as the reaction proceeded. The product was a mobile brown liquid, containing a small proportion of aluminium compounds in solution, and was accompanied by a considerable amount of carbonaceous sludge. The characteristics of the oil, after washing with alkali to free from aluminium compounds, and of the lubricating-oil fractions therefrom, have already been given (Tables III, IV).

With a catalyst containing a larger proportion of aluminium metal (30-gm. $AlCl_3$: 30-gm. Al) the polymerization reaction was considerably altered. As before, the activity of the catalyst did not diminish seriously with continued polymerization of ethylene, but the product contained no carbonaceous sludge and, in marked contrast to the former experiments, the liquid was of very unsaturated character. A higher proportion of dissolved aluminium compounds was present.

TABLE IX.

Distillation of Ethylene Polymers from 300° Reaction.

Catalyst:	30-gm. $AlCl_3$: 10-gm. Al.	30-gm. $AlCl_3$: 30-gm. Al.
Wt. of ethylene condensed in expt., gms.	735	560
Fraction :		
0–100°	8·3	16·8
100–200°	21·5	26·5
200°/760–150°/10 mm	25·8	22·0
150°/10 mm.–200°/10 mm.	15·0	10·4
Residue above 200°/10 mm.	29·4	24·3

TABLE X.

Unsaturation of Ethylene Polymers.

Catalyst.	Polymerisation Temp.	Fraction, ° C.	Addition Bromine Number.	Approx. Per cent. Unsaturation.
30-gm. $AlCl_3$: 10-gm. Al	100°	100–200	4·8	4
30-gm. $AlCl_3$: 10.gm. Al	200°	100–200	5·7	4·5
30-gm. $AlCl_3$: 10-gm. Al	300°	100–200	5·9	4·5
30-gm. $AlCl_3$: 30-gm. Al	300°	0–100	119	65
30-gm. $AlCl_3$: 30-gm. Al	300°	100–200	74	60
30-gm. $AlCl_3$: 30-gm. Al	300	200°/760 –150°/ 10 mm.	32	40

TABLE XI.

Engine Testing of Ethylene Polymers from 300° Reaction.

Catalyst:	30-gm. $AlCl_3$: 10-gm. Al.	30-gm. $AlCl_3$: 30-gm. Al.
I.P.T. distillation :		
I.B.P.	46° C.	39° C.
10%	81°	69°
50%	137°	126°
90%	203°	201°
Sp. gr., 60/60° F.	0·746	0·726
Blending octane number *	50	62

* 20% by volume in "A.2." petrol, S.30 engine.

The characteristics of the hydrocarbon polymers, in comparison with those from the catalyst of lower aluminium content, are given in Tables IX, X and XI. The high olefine content is surprising in view of the generally saturated character of catalytically produced ethylene polymers. The blending octane number is lower than that obtained by Bowen and Nash for the saturated *iso*paraffinic polymers from the normal aluminium chloride

polymerization of ethylene at 150° (octane number 77). This may indicate the presence of straight-chain olefines, being in line with the values, hexene-1, 80; heptene-1, 59·5; octene-1, 38·5; nonene-1, 15·0, found by Wilkinson.[31]

The nature of these polymerization products, in conjunction with the rapid cessation of catalytic activity at temperatures of 100–200° C. and the formation of aluminium ethyl chlorides, led to an investigation of the catalytic activity of these organo-metallic compounds of aluminium at higher temperatures. The results obtained, and their significance in relation to the data already given, are summarized in the following section.

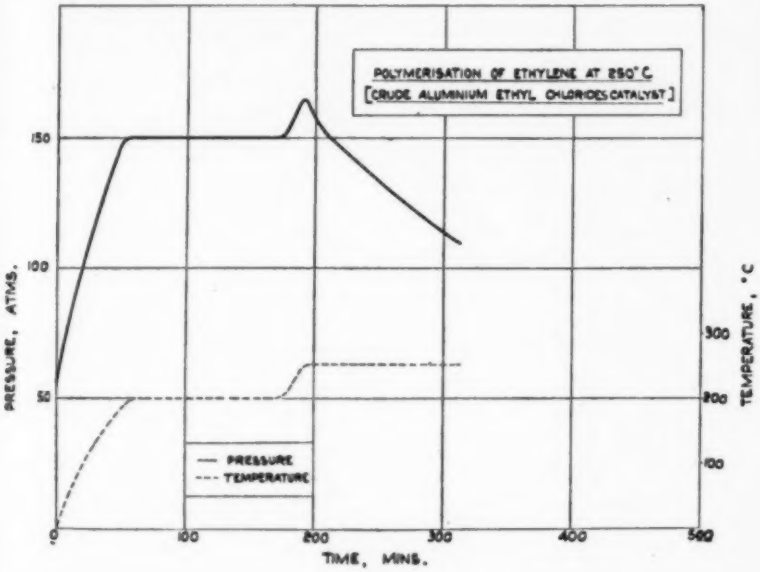


FIG. 5.

Catalytic Polymerization of Ethylene at 250–300° with Aluminium Ethyl Chloride Catalysts.

The catalytic action of crude aluminium ethyl chlorides of boiling range 85·5°/11 mm.–87·5°/10 mm. from the reaction of ethylene at 150° with a 30-gm. $AlCl_3$: 10-gm. Al (aluminium powder) catalyst was first investigated. The fraction contained 21·6 per cent. aluminium and 35·9 per cent. chlorine, and was regarded as a mixture of aluminium diethyl chloride and aluminium ethyl dichloride.[27] 33 gms. of the liquid (equivalent in chlorine content to 15 gms. of aluminium chloride) were introduced into the autoclave in a sealed glass bulb, which was subsequently fractured, and ethylene blown in to 53 atm. On raising the temperature no polymerization could be detected when maintained at 200° over a period of 2 hrs. At 250° the pressure fell steadily from a maximum of 165 atm. to 71 atm. over a period of 5 hrs, corresponding to the condensation of 95 gms. of ethylene (see Fig. 5).

Analysis of the residual gas (89 litres) showed it to be chiefly ethylene, with 17·1 per cent. higher olefines and 3·1 per cent. paraffins. The residual gas from the corresponding polymerization at 200° with aluminium chloride : aluminium catalysts contained no higher olefines. 129 gms. of a light-coloured mobile liquid product, reactive towards air and water, were obtained. Decomposition in petroleum ether solution with dilute alkali, followed by fractionation, gave a yield of 65·8 per cent. boiling above 100°/760 mm., on the initial liquid product. The lower-boiling fractions from this were very unsaturated, as may be seen from Table XII.

TABLE XII.

Fraction.	Per cent. by Weight on Product above 100°/760 mm.	Addition Bromine Number.
100–200°	15·1	55
200–150°/10 mm. . . .	10·7	38
Residue above 150°/10 mm. .	74·2	—

Polymerization at 300°.

Polymerization experiments were run at 300° using three catalytic materials under parallel conditions.

Experiment.		Catalyst.
A.	Crude aluminium ethyl chlorides.	34·3 gms. of the fraction 85·5–87·5°/10 mm., used in the 250° polymerization described above. Al = 21·6 per cent., Cl = 35·9 per cent.
B.	Aluminium-di-ethyl chloride.	43·5 gms. of the fraction 86·5–88°/10 mm. obtained by treatment of the above fraction (A) with excess sodium chloride. Al = 21·7 per cent., Cl = 27·9 per cent.
C.	Aluminium chloride-aluminium.	15·3 gms. of resublimed aluminium chloride (sublimed and pulverized in a sealed apparatus to avoid contamination with moisture) + 15 gms. of aluminium powder (grade C.A.1. British Aluminium Co.).

The catalysts were introduced into the autoclave in sealed glass bulbs, as before. Polymerization was carried out in two stages of approximately 1 hr. each. After the first polymerization the autoclave was allowed to cool and refilled with ethylene. Table XIII summarizes the experimental data

TABLE XIII.

Expt.	Catalyst.	Ethylene Pressure Atm.*			Product.		Ethylene Condensed, gms.
		Initial (cold).	Max. (hot).	Final (hot).	Liquid, gms.	Sludge, gms.	
A	Crude aluminium ethyl chlorides	49	171	30	437	24	427
B	Aluminium di-ethyl chloride	48	187	73	447	18	422
C	Aluminium chloride–aluminium	46	167	56	368	40	380

* Final cold pressure negligible in all cases.

obtained. The pressure–time–temperature graph for Expt. B. (aluminium diethyl chloride catalyst) is reproduced in Fig. 6, from which it is seen that, in common with the crude aluminium ethyl chlorides (Fig. 5), polymerization commences at a temperature between 200° and 250°, being inappreciable at 200° C.

The residual gas in the autoclave from each polymerization was collected and analysed on the Bone and Wheeler apparatus, the data being given in

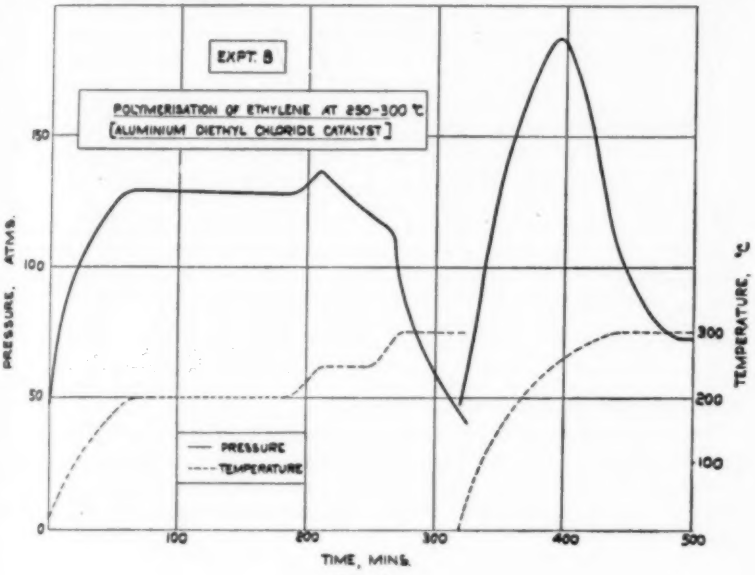


FIG. 6.

TABLE XIV.

	Experiment:		
	A. Crude Aluminium Ethyl Chlorides Catalyst.	B. Aluminium Diethyl Chloride Catalyst.	C. Aluminium Chloride–Aluminium Catalyst.
Higher olefines, %	7·2	33·8	25·4
Ethylene, %	2·2	8·3	6·0
Hydrogen, %	4·5	1·6	2·2
Paraffins, %	59·5	29·6	29·0
Nitrogen, %	26·6	26·7	37·4
Value of "n"	1·75	1·96	1·94
Volume of gas, litres	7	13	10

Table XIV. The lower olefine and higher paraffin content of the gas from Experiment A, and the similarity of the two other analyses, are noteworthy.

The product from each experiment was a mobile liquid containing a small

amount of sludge in suspension. The liquids from experiments B and C were both particularly volatile, that from B (aluminium diethyl chloride catalyst) being practically colourless. After centrifuging, washing with dilute sodium hydroxide solution and drying, the liquid products were distilled in an electrically heated Claisen flask assembly. The distillation data given in Table XV show the lower volatility of the product from experiment A and the close similarity between the products from experiments B and C.

TABLE XV.

Fraction, °C.	Experiment: A. Crude Aluminium Ethyl Chlorides Catalyst.	B. Aluminium Diethyl Chloride Catalyst.	C. Aluminium Chloride–Aluminium Catalyst.
Below 30° . .	1·8	16·5	13·8
30–100° . .	6·9	24·7	28·6
100–200° . .	26·8	33·4	33·4
200–150°/10 mm. .	27·5	15·4	12·1
150–200°/10 mm. .	14·8	5·2	4·0
Residue above 200°/10 mm. . .	21·7	3·6	7·2
Loss . . .	0·5	1·2	0·9

Examination of the Low-boiling Fractions.

Bromine numbers on the lower-boiling fractions are given in Table XVI, and show the high degree of unsaturation of the products from experiments B and C. Fractions from experiment A (crude aluminium ethyl chlorides catalyst) are more saturated, comparing closely with those for the same catalyst at 250° (Table XII).

TABLE XVI.

Fraction, °C.	Experiment: A.	B.	C.
30–100°	114	165	164
100–200°	60	105	108
200–150°/10 mm. . . .	32	58	56

The fraction distilling below 30°, from experiment B, was distilled in the Podbielniak apparatus. 60–70 per cent. distilled at a temperature of —6° C. (corresponding either to butene-1 or *iso*butylene) with no evidence for any C_3 hydrocarbons. For further identification, the fraction was brominated by the method of Manning, King and Sinnatt.[32] Complete absorption of the vaporized hydrocarbon showed the absence of any saturated components. A yield of 69 gms. of crude dibromides was obtained from 23 gms. of the hydrocarbon. By fractional distillation at reduced pressure 75 per cent. distilled between 66·5 and 69·5°/30 mm. At atmospheric pressure this had a corrected boiling point of 162–164°, which corresponds fairly

closely with the reported figure of 165·6–166° for butene-1 dibromide, in contrast to the figure of 148–149° for *iso*butylene dibromide. Identical data were obtained for the corresponding fraction from experiment C, and it was concluded that the lowest-boiling fraction from both these experiments (with aluminium diethyl chloride, and with aluminium–aluminium chloride catalysts) was essentially butene-1.

The combined 30–200° distillates from each experiment were separately fractionated through a 50-cm. vacuum-jacketed Dufton-type column,

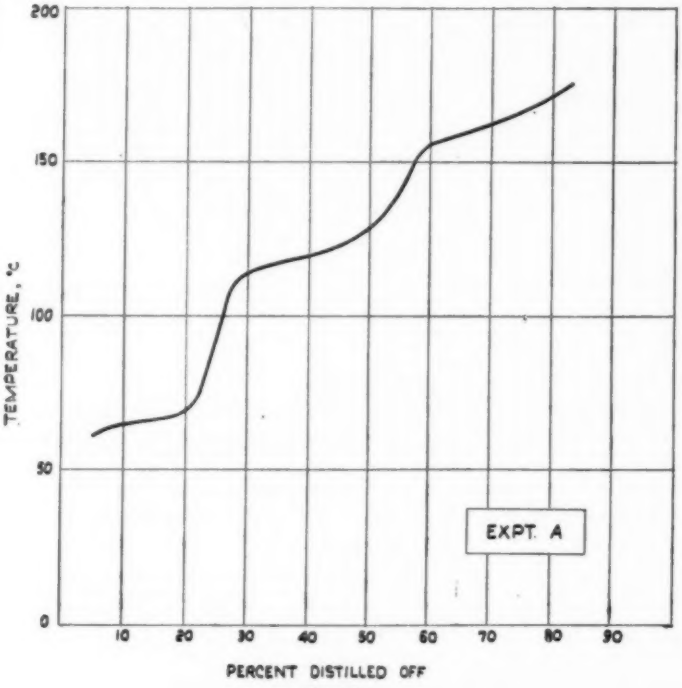


FIG. 7.

DISTILLATION OF ETHYLENE POLYMERS.
CRUDE ALUMINIUM ETHYL CHLORIDES CATALYST AT 300° C.

capable of good fractionation. 50 ml. were distilled at 1–2 drops per second, a lower rate being maintained when changing from one temperature plateau to the next. The data obtained (uncorrected) are reproduced as distillation curves in Figs. 7, 8 and 9, and provide a particularly interesting comparison. The curves for the experiments using the aluminium diethyl chloride and aluminium–aluminium chloride catalysts are closely similar, and show exceptionally well-marked plateaus at temperatures corresponding to the even carbon atom groupings, C_6, C_8 and C_{10}, with a complete absence of the C_5, C_7 and C_9 groupings.

Taken in conjunction with the data obtained for the lowest-boiling

distillate (butene-1), and with the exceptionally high bromine values of these fractions, it is evident that in the polymerization of ethylene at 300° with either aluminium diethyl chloride, or with aluminium chloride and an excess of aluminium, the reaction follows a simple chain mechanism giving dimers, trimers and higher chain polymers of the original ethylene molecule.

The same general characteristics are shown in the distillation curve for the crude aluminium ethyl chloride catalyst, but the plateaus are much less

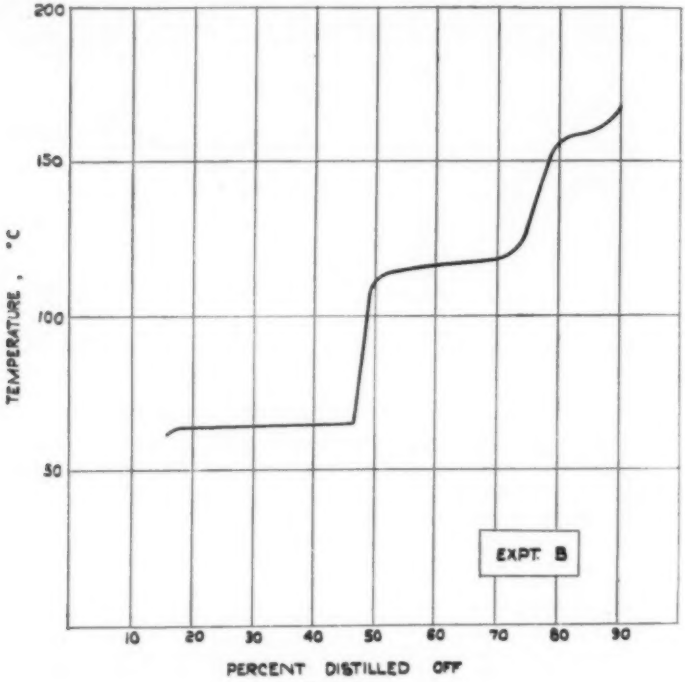


FIG. 8.

DISTILLATION OF ETHYLENE POLYMERS.
ALUMINIUM DIETHYL CHLORIDE CATALYST AT 300° C.

clearly defined, indicating, probably, isomerization, the appearance of odd-carbon atom groupings, and some degree of saturation.

Higher-boiling Fractions.

The data for the residual fractions from these 300° polymerizations, and for that from the 250° reaction, are summarized in Table XVII.

Considering the action of the crude aluminium ethyl chlorides fraction at 250° and at 300° (experiment A), the proportion of high-boiling constituents decreases with increase in reaction temperature, accompanied by a parallel decrease in viscosity. Both viscosity indices are higher than any recorded in the polymerization work at lower temperatures, whilst the viscosity

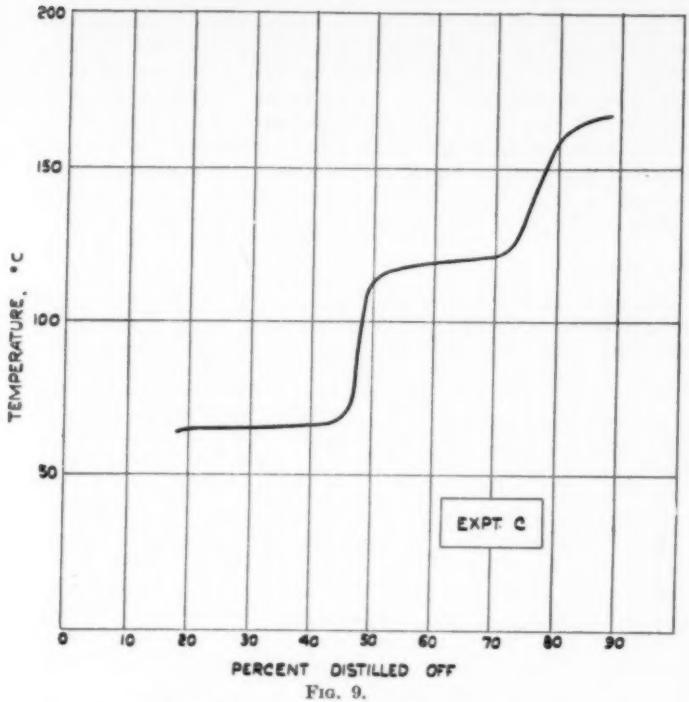


FIG. 9.

DISTILLATION OF ETHYLENE POLYMERS.
ALUMINIUM CHLORIDE—ALUMINIUM CATALYST AT 300° C.

TABLE XVII.

Properties of Residual Fractions from Polymerization of Ethylene.

	Crude Aluminium Ethyl Chlorides Catalyst.	A. Crude Aluminium Ethyl Chlorides Catalyst.	B. Aluminium Diethyl Chloride Catalyst.	C. Aluminium Chloride + Aluminium Catalyst.
Reaction temperature, ° C.	250°	300°	300°	300°
Fraction	Above 150° at 10 mm.	Above 200° at 10 mm.	Above 200° at 10 mm.	Above 200° at 10 mm.
Per cent. of product . .	67·5	21·7	3·6	7·2
Viscosity (centistokes) :				
At 100° F. . . .	193	52·3	45	—
At 210° F. . . .	15·4	6·6	—	169 (200° F.)
Viscosity index . .	86	80	—	—
Sp. gr. 60/60° F. . .	0·851	0·860	0·857	—
Viscosity gravity constant.	0·758	0·796	0·797	—
Carbon hydrogen analyses :				
Carbon, % . . .	—	84·87	86·10	87·95
Hydrogen, % . .	—	12·86	13·50	12·14
Total, % . . .	—	97·73	99·60	100·09

gravity constant of the 250° reaction temperature oil recalls the similar low values obtained for olefine polymers produced at low temperatures.

With the aluminium diethyl chloride catalyst (experiment B) the residual fraction has decreased to a very small amount, whilst retaining a similar viscosity and gravity. In contrast, that from experiment C ($AlCl_3$: Al catalyst) is greater in amount and is extremely viscous. The low hydrogen content of this would be expected if this residual fraction were regarded as the source of the hydrogen utilized in the formation of the aluminium ethyl chlorides in the initial stage of the reaction.

Discussion.

The close agreement between the two experiments using aluminium diethyl chloride and aluminium chloride with an excess of aluminium metal, respectively, is particularly noteworthy. In the latter case it appears that the initial reaction is the conversion of the aluminium chloride into aluminium ethyl chlorides (in the presence of ethylene and excess aluminium metal), with the simultaneous formation of viscous hydrocarbon polymers. The formation of these polymers is shown by the presence of 7·2 per cent. of an extremely viscous residual fraction in the final product (experiment C). The subsequent catalytic activity of the aluminium ethyl compounds formed is identical *not* with that of the crude aluminium ethyl compounds formed by separate reaction at lower temperatures, but with that of the aluminium diethyl chloride, obtained by sodium chloride extraction of this crude product. The presence of a large excess of aluminium metal in the reaction appears responsible for this, the aluminium chloride probably being completely converted into the aluminium diethyl chloride under the existing conditions. With less aluminium present the reaction has been shown to take a different and more complex course. Thus the experiment reported, using a 30-gm. $AlCl_3$: 10-gm. Al catalyst at 300°, gave rise to a saturated product, with evidence of cracking and decomposition reactions leading to the formation of coke, whereas under similar conditions but with a larger excess of aluminium, the products were highly unsaturated, with an entire absence of coke.

The polymerization reactions involving the crude aluminium ethyl chloride fraction are also more complex. Apparently at high temperatures the components of high chlorine content in this catalyst (presumably aluminium ethyl dichloride) function in a manner somewhat resembling that of aluminium chloride alone. The reaction may be regarded as a two-stage process: (1) the polymerization of ethylene to relatively long-chain olefine polymers which is the reaction observed with aluminium diethyl chloride, and (2) the secondary polymerization of these olefines to lubricating oil fractions of comparatively high viscosity index by the aluminium ethyl dichloride. The presence of the aluminium ethyl dichloride, like aluminium chloride, apparently leads to a certain amount of destructive cracking and isomerization to saturated hydrocarbons.

It is probable that the catalytic polymerization of ethylene at 250–300° C. in the reactions studied is associated with the presence of free ethyl radicals. The evidence for this is twofold. It has recently been shown that ethylene is polymerized by free (*i.e.*, nascent) alkyl radicals formed through the incipient thermal decomposition of such compounds as lead tetraethyl and

azomethane. Taylor and Jones [33] studied the vapour-phase decomposition of lead tetraethyl in the presence of hydrogen and ethylene mixtures. In a flow experiment at 325° a liquid condensate was obtained, containing 80 per cent. unsaturateds, boiling at approximately 75°. This condensate was shown to have the empirical composition $CH_2)_n$, but the analytical results are insufficient for further comparison with the data obtained in the present work. The reaction is analogous to that induced by α-particles, by activated mercury atoms and by the silent electric discharge. In this connection, using the silent electric discharge under controlled conditions, Mignonac and Saint Aunay [34] were able to isolate butene-1 and hexene-1 from the polymerization of ethylene.

The results of Taylor and Jones have been confirmed by Cramer,[35] using liquid-phase conditions (under pressure) with benzene as solvent. At 260–275° small quantities of liquid olefine polymers were obtained, but again analytical results are lacking. More recently Rice [36] has reported that ethylene is rapidly polymerized by free methyl radicals from the decomposition of azomethane at 300° C.

According to Roux and Louise,[37] thermal decomposition of aluminium triethyl commences at temperatures of the order of 250° C., in striking agreement with the temperature of initial polymerization found in the present work.

The mechanism of the polymerization of ethylene by free alkyl radicals is still obscure, but Cramer considers the evidence to be in favour of the theory advanced by Taylor and Jones. It is assumed that by a three-body collision between two molecules of ethylene and one free radical, free radicals of higher " molecular " weight are formed as the inital step. These may then react either with one another to give saturated paraffin molecules, or with a molecule of ethylene to give an olefine of higher molecular weight, together with a free radical of lower complexity. The latter reaction is considered more probable and may be represented as :

$$(C_2H_5) + C_2H_4 + C_2H_4 \longrightarrow (C_4H_9) + C_2H_4$$
$$(C_4H_9) + C_2H_4 + C_2H_4 \longrightarrow (C_6H_{13}) + C_2H_4$$
and so on
$$(C_6H_{13}) + C_2H_4 \longrightarrow C_6H_{12} + (C_2H_5)$$

By this mechanism the products of reaction would be expected to comprise a range of olefine polymers, containing even numbers of carbon atoms, with no marked proportion of saturated molecules. These results are, in fact, found in the present experimental work, and there appears every probability that the polymerization observed is due to free ethyl radicals from the incipient thermal decomposition of the aluminium ethyl chlorides present.

Conclusion.

The reactions described in this paper open up a particularly interesting field of research. Until quite recently, relatively little published data on organo-metallic alkyl compounds of aluminium were available. Since the publication of the authors' first communication,[27] however, a brief abstract of work by Grosse and Mavity [38] has appeared, which extends our knowledge of these aluminium compounds. These investigators confirm the existence of a series of chloro-derivatives of the aluminium alkyl

and aryl compounds, and the formation of crystalline addition compounds with alkali metal halides (Hall and Nash [27]). Aluminium diethyl chloride and aluminium ethyl dichloride were isolated, the former compound having a b. pt. of 215·5° at 760 mm., a figure in very close agreement with that of 214–215° obtained in the present investigation.[27]

So far as the authors are aware, no work has been reported describing the formation of organo-metallic ethyl derivatives of aluminium in any olefine condensation or polymerization reaction. The high yields obtained, the simplicity of the reaction, and the ease by which the alkyl derivatives may be recovered by simple fractional distillation in vacuum, present possibilities for further development in this field. The use of these compounds as synthetic derivatives is, to some extent, limited by the pronounced condensing action of aluminium alkyl compounds (in comparison, for example, with zinc alkyls and the Grignard reagent), but a number of reactions characteristic of the reactive metallic alkyl derivatives are possible and have been investigated. It is not yet known to what extent the formation of such compounds proceeds in the case of the higher olefines, but evidence for the formation of butyl derivatives of aluminium chloride has been found.

The polymerization of ethylene at higher temperatures by the aluminium ethyl compounds, or more simply by aluminium chloride–aluminium catalysts, is of considerable interest, both from its theoretical significance and from its use as a particularly simple reaction for the production of high yields of simple dimeric, trimeric and tetrameric polymers of ethylene. Hexenes and octenes produced in this manner may be separated with comparative ease by fractional distillation, and are available for further polymerization to lubricating oils, or as intermediates for the synthesis of a range of olefine derivatives.

Acknowledgment.

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Department of Oil Engineering and Refining.
University of Birmingham

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THE PROPERTIES OF ASPHALTIC BITUMEN IN RELATION TO THE ROAD.*

By F. H. Garner, Ph.D., F.I.C. (Member).

Summary.

The evaluation of various asphaltic bitumens for road purposes must be based on the physical and chemical properties of the bitumen, but the behaviour in use is also influenced by the character and proportions of the road aggregate with which the bitumen is mixed and by the methods of mixing and of laying on the road. Methods of test for determining those properties of bitumen aggregate mixtures which are most important for road work have not yet been standardized, nor have such tests been adequately checked against road experience; hence there is a wide gap between physical and chemical properties of asphaltic bitumen and knowledge of their influence on road behaviour.

In this paper a summary is given of the present knowledge of the chemistry of asphaltic bitumen and of its physical properties. The physical properties which are of most importance are consistency and variation of consistency with temperature; consistency is measured by such tests as penetration or melting point, but more recently viscosity methods have been developed which have been particularly helpful in understanding the importance of the part which structure plays in determining the physical properties of asphaltic bitumen.

The durability of the road in which asphaltic bitumen is used depends on the effect of weathering; weathering is dependent not only on the nature of the chemical compounds present in the bitumen which influence such properties as adhesion of the bitumen to the road aggregate, but also on the physical properties, such as consistency.

The water-proofing qualities of bitumen binders have supplied an essential part of the "covering impenetrable to rain" required by McAdam in 1822 for the surfacing of roads. After stressing that it is native sub-soil which really supports the weight of traffic and does in fact carry the road and the carriages also, he states that a covering impenetrable to rain must be placed over it, experience having shown that if water passes through a road and reaches the native soil, the road, whatever may be its thickness, loses its support and goes to pieces.[1]

In bituminous road surfaces consideration must be given to the following:—

(1) Bituminous binder.
(2) Road aggregate.
(3) Composition of the mixture—binder and aggregate.
(4) Manufacture of bituminous mixture.
(5) Laying on the road.

In the last three of these, the physical and chemical properties of the bituminous binder may not be of most importance in determining the durability of the road in use. The correct proportions of the mixture of

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binder and aggregate must be determined by traffic and temperature conditions, since failure and success may equally well result with the same mixture on light and heavy traffic roads; a deficiency in binder content may lead to road failure under winter conditions or an excess to slippery road surfaces in summer. Similarly, in the manufacture of the bituminous mixtures, inefficient temperature control often results in overheating the bituminous binder and leads to the use of too hard material even if its essential binding qualities are not destroyed. In laying the mixture on the road, weather conditions and mechanical handling of the mixture are of the greatest importance, as is often noted even in the reports of official trial sections where the same material laid at different times has given entirely different results in practice. All these points have to be considered in every type of road surfacing, but this paper refers mainly to number 1, bituminous binder, and the relations between the physical and chemical properties and the performance of asphaltic bitumen from the standpoint of durability and use in the making of roads.

It has been pointed out that Richardson, in his book on "The Modern Asphalt Pavement," quoted a letter written in 1893 in which the following question was asked: "What is the real test of standard or quality which will give the value of an asphalt for paving processes?"

The chemist to whom this letter was addressed made the following reply: "The real and final test of the quality of an asphalt for paving purposes is actual trial for a proper length of time. Proper chemical and physical tests of a new variety of asphalt may strongly indicate its probable value as a paving material, but these tests, although of great assistance in forming an opinion, really only show the advisability of submitting the asphalt to the final and infallible test of actual trial."

E. F. Kelley, Chief of Division of Tests, U.S. Bureau of Public Roads, states [2] that it seems to be a well-established fact that the service characteristics of a paving asphalt cannot be accurately defined by any of the tests which are now in use and that it is the opinion of many well-informed engineers and technicians that the quoted statement is practically as true to-day as it was in 1893.

Of the whole series of products derived from petroleum, it is found that the higher the boiling point the greater is the complexity of the product. Thus, from the lightest fractions, such as are present in gasolines, it is possible to separate individual hydrocarbons of the various groups, paraffin, olefine, naphthene, and aromatic. As the boiling point increases the complexity becomes greater and in the higher boiling compounds it is even a matter of great difficulty to ascertain what types of hydrocarbons are present. Asphaltic bitumen can be considered as the highest boiling product from petroleum and is the most difficult product to separate into chemical compounds or groups of chemical compounds.

Similarly, it is possible from the results of purely laboratory investigations to assess the value of a gasoline (as regards its performance in use as fuel in a spark-ignition engine), but the higher boiling of the product, the less can purely physical and chemical tests be used for this purpose; thus, with motor lubricating oils duration tests using engines are necessary to determine performance qualities. For asphalts a series of physical tests have been devised, such as penetration, viscosity and softening point, which

serve to describe the product. These laboratory tests must be supplemented by mechanical tests on the bitumen aggregate mixture and, if interpreted in comparison with extensive road experience, entirely satisfactory road surfaces can be constructed. With new types of construction there is, however, much greater difficulty owing to the lack of fundamental knowledge of the underlying principles. A number of mechanical tests have been devised for bitumen aggregate mixture but the most recent report of the Road Research Board (for the year ending March 31st, 1937) [3] points out that "no widely accepted tests exist at present which are applicable to more than a very limited range of bitumen mixtures; and those which have been used do not give a value for the material which can be regarded as a definite physical constant: they simply measure resistance to deformation under certain arbitrary conditions of loading or deformation." In order to express the mechanical properties of bituminous surfacing materials in the simplest possible terms, the tests which have been used in the Road Research Laboratory are those involving the application of constant stress, and comprise a beam test, a tensile test and a parallel plate shear test. In all these tests deformation/time curves are obtained. Considerable care has been given to the development of a technique for producing the samples for test. Each of these tests has a special application—the beam test is very simple and can be used for measurement of the effects of ageing; the shear test is adaptable to materials which deform readily; whereas the tensile test is suitable for a wider range of materials.

There is, however, a wide gap, which is continually being narrowed by research, between this type of laboratory test and actual road behaviour; in order to achieve more rapid results, road machines, in which bitumen-aggregate mixtures can be subjected to traffic, are in extensive use as a connecting link between such tests and road practice. One of the first of these machines was that installed in the National Physical Laboratory in 1912, now transferred to the Road Research Laboratory in Harmondsworth. However, caution has to be exercised in translating the results from road machines to the road, since factors such as traffic load and speed, and weather conditions again are very important and may cause variations. These points have been emphasized in order to stress the very great difficulty which underlies any rapid testing of bituminous materials in order to assess their value for road purposes and particularly as a comment on the statement quoted from Clifford Richardson.

The properties of asphaltic bitumen are largely dependent on its complex structure, and it is proposed to refer first to its components, oily constituents, asphaltic resins, asphaltenes and more insoluble materials, such as carbenes, and then to the chemical composition of the bitumen and its components. The most important physical properties dependent on consistency or flow properties (viscosity, penetration, softening point, ductility and elasticity) are then considered, followed by the chemical properties—changes produced by exposure to light and oxidation. It is not possible to effect a sharp separation under these headings since much information of the structure of asphaltic bitumen has been derived from consideration of the flow properties. The flow properties of bitumen-aggregate mixtures are not discussed in this paper and the interrelation of bitumen and aggregate is only considered in reference to adhesiveness.

The increasing knowledge of the physical and chemical properties of asphaltic bitumen with increasing knowledge of its structure, is providing a sound basis for the practical applications of asphaltic bitumen and asphalts.

Components of Asphaltic Bitumen—Asphaltenes, Asphaltic Resins and Petrolenes.

Since asphaltic bitumen is essentially a product of very high boiling point, it is only possible to effect a partial separation by distillation, even under a high vacuum, because substantial proportions cannot be distilled even under these conditions. Separation has, therefore, been effected chiefly by means of solvents in which part of the bitumen is soluble and part insoluble. For asphaltene determination light petroleum spirit, such as normal benzine or the more rigidly defined solvent specified by the Institute of Petroleum may be used.[4] For asphaltic resin determination, the benzine solution of bitumen, freed from asphaltenes, is mixed with an absorbent clay or silica gel and the oil portion or petrolenes extracted by suitable solvents such as chloroform, leaving the asphaltic resins in the clay. Thus asphaltic bitumen can be separated into asphaltenes, asphaltic resins and oily constituents or petrolenes. If the bitumen is separated into asphaltenes and oily constituents only, then the name malthenes is often applied to the latter (petrolene plus asphaltic resins.)

It is, however, important to note that the separation which has been effected is only a grouping somewhat similar to sieving operations on crushed rock or road aggregate in which particles of various sizes have been separated. The chemical composition of the various sizes of separated rock may be different and this applies equally to the products separated from asphaltic bitumen, and further the proportions of the various groups present will vary widely in materials from different sources; in both cases further sub-division of the groups can be effected by suitable means.

More insoluble substances than asphaltenes can be separated from some asphaltic bitumens by suitable solvents, such as "carbenes" by carbon tetrachloride or "carboids" by carbon disulphide.

Since solvents and methods of separation have not been rigidly standardized, analytical results obtained by different workers vary rather widely, so that it is preferable to limit any comparison of asphaltenes, asphaltic resins and oily constituents in different asphaltic bitumens to work done by one laboratory.

Table I shows results quoted by C. M. Baskin [5] for a number of steam-refined, blown and cracked asphaltic bitumens. The wide variation of asphaltene contents will be noted, ranging from 4 per cent. in the Californian light Flux to 13·6 per cent. in a similar Mexican Flux. Both of these bitumens have been widely used in road-work with entirely satisfactory results. The asphaltene content and asphaltic resin content increases with increasing softening point or decreasing penetration for asphaltic bitumens from the same crude. Blown bitumens contain more asphaltenes and less oily constituents than steam-refined asphaltic bitumens; the ratio of asphaltenes to asphaltic resins is much higher in blown bitumens than in steam-refined bitumens. The cracked blown bitumens shown in the table have a relatively high proportion of asphaltenes to resins and a very high content of oily constituents.

For comparison, the composition of the bitumen from Trinidad Lake asphalt is apparently :—

Oily constituents	31%
Asphaltic resins	23%
Asphaltenes and Carbenes	46%

but this material is, of course, of a higher softening point (150° F.) than any of the steam-refined bitumens given in Table I.

Attention has recently been directed to a test in which asphaltic bitumen mixed with a suitable solvent is placed on a piece of filter paper and the presence of insoluble material can be detected by the formation of a ring.

TABLE I.

Source of Asphalt.	Softening Point B. & R. ° F.	Penetration. 100 gms. at 77° F.	Asphaltenes. %.	Asphaltic Resins. %.	Petrolenes. Oily constituents. %.
Steam Refined.					
Panuco	85	T.S.	13·65	26·64	59·20
Panuco	108	160	16·40	30·77	52·83
Colombian	107½	189	6·90	20·40	72·60
Illinois	102	235	5·24	35·12	59·49
Californian	81	T.S.	4·04	34·41	60·71
Quire Quire	102½	190	3·19	23·88	70·65
Cracked.					
High Pressure C.C. Tar	105	150	14·43	9·32	76·15
Low Pressure C.C. Tar	103	183	11·56	13·92	74·52
Air Blown.					
Panuco	155	42	30·25	27·30	41·83
Panuco	148	40	26·84	28·36	44·88
Colombian	144½	40	16·38	29·93	53·69
Illinois	147½	39	13·66	36·76	49·58
Californian	133	30	18·32	28·30	52·80
Quire Quire	144	21	19·16	28·54	52·30
Cracked and Air Blown.					
High Pressure C.C. Tar	148	16	26·97	4·45	68·58
Low Pressure C.C. Tar	148	22½	22·75	8·24	69·01

The difference between 100% and the sum of asphaltenes, asphaltic resins and oily constituents is presumably saponifiable constituents.

This type of test has, of course, been widely used for other purposes, but it has recently been applied to asphaltic bitumens by Oliensis.[6] Some straight-run bitumens show the presence of insoluble material [7] in this test, but cracked materials in particular tend to exhibit lack of homogeneity due to the presence of material insoluble in the naphtha used. This test is of doubtful value as an indication of the quality of an asphaltic bitumen.

The physical properties of asphaltic bitumen, however, cannot be explained from the idea that asphaltic bitumen is merely a mixture of various groups of compounds, and it is to Nellensteyn [8] in particular that credit is due for the present attention paid to the importance of structure.

Nellensteyn's theory postulates that asphaltenes consist of a carbon

nucleus surrounded by protective bodies, and asphaltic bitumen thus consists of carbon surrounded by layers of hydrocarbons in which the ratio of carbon/hydrogen becomes progressively lower; the outermost layer of this dispersed phase will be the same as that of the oily medium (dispersing phase). Graphitic carbon has been indicated to be present in asphaltenes by X-ray diagrams. This theory, however, has not been accepted by other workers. Mack [9] pointed out that if asphaltenes were composed of free carbon plus protective bodies, it would be anticipated that these would be of a large particle size but that actually the molecular weights of a series of typical bitumen ranged from only 1500 to 1800: further evidence of the relatively small size is that under suitable conditions asphaltenes can be dialyzed. Pfeiffer and van Doormaal [10] state that it is unproved, and on the strength of ultra-microscopic examination scarcely likely, that the nucleus of the dispersed phase should consist of elementary carbon.

Asphaltic bitumen consists of asphaltenes partly suspended and partly dissolved in an oily medium, and its physical properties are determined by the chemical compositions of these components, asphaltenes and malthenes, as will be discussed later under consistency. Asphaltic resins, intermediate between asphaltenes and the oily medium (petrolenes) also play an important part in determining the physical properties of the asphaltic bitumen. It must be remembered that all three groups merge into one another and that the separations effected by solvents are incomplete. Hillman and Barnett [11] point out that when a cracked bitumen containing carbenes was mixed with asphaltic resins from the same bitumen, no carbenes could be found in the mixed bitumen by the usual methods.

Chemical Composition.

In addition to carbon and hydrogen, sulphur, nitrogen and oxygen compounds are present in varying proportions in different asphaltic bitumens; it is sometimes assumed that hydrocarbons are the only important compounds present, but the sulphur compounds in particular in some bitumens are present in large proportions. It is proposed first to consider the chemical composition of the asphaltenes, asphaltic resins and petrolenes, and then the compounds in asphaltic bitumen other than hydrocarbons.

Asphaltenes.

The carbon/hydrogen ratio (atoms of carbon to atoms of hydrogen) may vary from about 1 : 1·7 in the oily constituents to about 1 : 1 for the asphaltenes.

Table II.

Asphaltenes from Asphaltic Bitumen.

	Steam Refined and Air Blown.	Cracked.
Molecular Weight . .	1200–1800*	500–800
Atoms C : Atoms H . .	*ca.* 1 : 1 †	*ca.* 1 : 0·88

* Spielmann and Hughes,[14] p. 35, quote molecular weights for asphaltenes from blown bitumens as high as 4690.

† References [9, 12, 13, 14].

It will be seen from Table II that asphaltenes from cracked products

have lower molecular weights and higher C: H ratios than those from steam-refined or air-blown bitumens.

The high carbon ratio of the asphaltenes shows that hydrocarbons of cyclic character are present, although these are obviously different from the highly condensed benzene ring hydrocarbons, which are crystalline solids of high melting point. Pfeiffer and van Doormaal [10] considered asphaltenes to be predominantly aromatic or hydro-aromatic (naphthene) compounds; in agreement with which Hillman and Barnett [11] have shown that the asphaltenes in cracked asphalts probably contain both aromatic and naphthene rings. Asphaltenes always appear to contain sulphur and possibly oxygen and nitrogen compounds in addition to hydrocarbons. From a Mexican bitumen of 170 penetration Pöll [12] separated asphaltenes by different methods as shown in Table III.

TABLE III.

Asphaltenes. %	C. %	H. %	S. %	O and N by difference. %
(*a*) 26·02 . . .	82·64	8·61	8·66	0·09
(*b*) 18·60 . . .	83·45	7·37	8·83	0·35
(*c*) 4·62 . . .	78·51	7·36	14·07	0·089

The lower the yield of asphaltenes the more free are the asphaltenes from oily constituents. Table III shows that when only 4·62 per cent. asphaltenes were obtained (less than $\frac{1}{5}$ of (*a*)), there is a very marked increase in sulphur content and lowering of carbon content. This may indicate that sulphur compounds are an important component of the asphaltenes in Mexican bitumens.

Asphaltic Resins.

Very little is known as regards the chemical composition of the asphaltic resins, but it is believed that they consist essentially of polycyclic compounds and are intermediate in character between the oily constituents and the asphaltenes.[14] The molecular weights of the asphaltic resins are dependent on the molecular weights of the petrolenes and are lower than asphaltenes.[15]

Petrolenes.

The petrolenes are high boiling oils of wider distillation range than is usually found in lubricating oil distillates; in different asphaltic bitumens they vary widely in chemical composition and consequently in solvent power. Mair and Willingham [16] find mainly ring compounds present in high boiling fractions from petroleum ranging from naphthenes with one or more rings with attached alkyl groups to hydrocarbons containing both naphthene rings and one aromatic ring.

A normal group of hydrocarbons present in petroleum and in the petrolenes of asphaltic bitumen is paraffin wax. There has been a tendency to concentrate attention on the proportion of paraffin wax as an indication of the quality of the bitumen; there is, however, no justification for the statement that the lower the percentage of paraffin wax the higher the quality of the bitumen, but if paraffin wax is present in excessive proportion so that it

can crystallize out, it will undoubtedly modify the structure of the bitumen and may lead to brittleness at low temperatures, and consequently destroy the essential plastic qualities of asphaltic bitumen. Spielmann quotes figures, however, indicating that as much as 4 per cent. may have little influence on the ductility and penetration of asphaltic bitumen.[17]

Sulphur Compounds in Asphaltic Bitumens.

There is little known as regards the type of sulphur compounds which are present, but in some asphaltic bitumens where the sulphur content is over 5 per cent. the proportion of such compounds present must be very high. In such bitumens each of the components, asphaltenes, asphaltic resin and petrolenes, has a high sulphur content [12] (Table IV).

TABLE IV.

	%	Carbon. %	Hydrogen %	Sulphur. %	Oxygen and * Nitrogen by difference. %	Ash. %
			Pöll.[12]			
Mexican Bitumen of 170 Penetration	—	82·93	10·37	6·20	0·50	—
Asphaltenes	18·60	83·45	7·37	8·83	0·35	—
Asphaltic Resins †	19·44	82·56	9·70	7·15	0·59	—
Oil Resins †	20·34	82·83	10·14	6·83	0·20	—
Oil	41·22	83·75	12·01	4·27	—	—
	99·63					
			Thurston and Knowles.[13]			
Mexican Bitumen of 238 Penetration	—	85·05	10·38	6·10	—	0·27
Asphaltenes	28·0	79·60	7·79	8·09	3·92	0·50
Asphaltic Resins †	15·7	82·19	10·38	8·55	—	—
Oil Resins †	22·0	82·7	10·89	5·60	0·81	—
Oil	34·0	85·39	11·39	4·04	—	—
	99·7					
			Sakhanov [18]*—Russian Bitumens.*			
Asphaltenes	—	85·3	6·4	0·6	9·7	—
Asphaltic Resins	—	84·12	9·92	0·64	5·32	—

* A blank in the column oxygen and nitrogen indicates that carbon, hydrogen, sulphur and ash add to over 100.

† Asphaltic resins were divided by Pöll into these two components.

Knowledge of the sulphur compounds present is limited to the petrolenes, but thiophenes and thiophanes are present and correspond to aromatic and naphthene hydrocarbons in structure, and with a sulphur atom in the ring in the place of one of the CH_2 groups. The thiophene compounds are similar in properties to aromatic hydrocarbons (although there are only five atoms in the ring), so that it is a matter of some difficulty to effect a separation, but the thiophanes are more similar to the aliphatic sulphides, and can readily be separated in the form of mercury double salts.[18]

Oxygen and Nitrogen Compounds in Asphaltic Bitumen.

Oxygen and nitrogen compounds are usually present in relatively small proportions in asphaltic bitumens, but in view of the active chemical behaviour of their compounds the proportion present appears to be of importance. Thurston and Knowles [13] found up to 6 per cent. of oxygen and nitrogen in asphaltenes as compared with negligible proportions in the asphaltic resins and oily constituents (see Tables III and IV); Sakhanov, however, in Russian bitumen [15] found over 5·3 per cent. of oxygen and nitrogen in asphaltic resins. It will be seen in Table IV that none of the published figures for oxygen and nitrogen contained is very reliable, but there is no doubt that both oxygen and nitrogen do occur in varying proportions in both asphaltenes and asphaltic resins.

Naphthenic acids are a normal constituent of petroleum, and are present in different asphaltic bitumens in widely varied proportions. J. von Braun [19] has suggested that the whole of the acids which can be isolated from petroleum should be included in the term naphthenic acids, and this will comprise, with phenols, all the oxygen compounds present in asphaltic bitumen of which the structure is known. In naphthenic acids (apart from aliphatic acids) a carboxyl group is attached to a side chain, which is in turn attached to a ring structure, containing *cyclo*pentane, more or less heavily substituted with alkyl radicals. Reference has been made in the literature to asphaltogenic or asphaltous acids, but the terms asphaltogenic acid, and particularly asphaltic anhydrides, are so loosely defined and so indefinite from the chemical point of view that they might well fall into disuse.

The percentage of nitrogen in various bitumens is given by Mabery and Byerley [2] as varying from 0·18–0·64 per cent. as against 1·88–2·39 per cent. of oxygen, whilst in the asphaltenes from hard steam-refined Mexican bitumen 1·16 per cent. nitrogen and 0·73 per cent. oxygen was found.[13] Nitrogen bases in small but varied proportions represent the compounds of nitrogen which have been identified in petroleum. These bases contain quinoline and pyridine rings and *cyclo*pentane rings [2] (C. Ellis and S. R. Bailey).

Apparently all the hydrocarbons, sulphur, oxygen and nitrogen compounds present in asphaltic bitumen are largely of cyclic structure. In the hydrocarbons five- and six-atom ring structures are present, whereas in the oxygen compounds—naphthenic acids—only five-atom rings have been shown to be present. In the sulphur and nitrogen compounds ring structures are again present, the sulphur compounds being derived from the five-atom ringed thiophene or thiophane with a sulphur atom in the ring, and the nitrogen compounds from pyridine or quinoline with a nitrogen atom in the ring.

Physical Properties—Consistency.

Penetration and softening point (ball and ring) are most widely used for determining the consistency of asphaltic bitumen, but these empirical tests are influenced by other factors than viscosity, such as adhesiveness.

The consistency or flow properties of asphaltic bitumen over a range of temperatures are of fundamental importance, since they influence the manufacture and use of the material, the selection of the grade to be used in

bitumen–aggregate mixtures, the manufacture and laying of the bitumen mixture, and the durability of the road surface.

The durability of the paving surface depends on the variation of consistency with temperature which determines : (*a*) the behaviour of the pavement at low temperatures, and if unsuitable, may lead to cracking; (*b*) instability at high atmospheric temperatures which may cause either deformation of the road surface, giving uneven riding surfaces, or flow of bitumen to the surface, leading to slippery surfaces. In such failures not only the bitumen, but also the bitumen–aggregate mixture must be considered so that too much stress must not be placed on the properties of the bitumen alone.

Flow Properties and Composition.

The flow properties are dependent on the nature of the asphaltenes and oily constituents, since asphaltic bitumens may be on the one hand viscous liquids and, on the other, complex liquids showing anomalous flow or exhibiting plasticity to some extent.

True liquids are continuously deformed when subjected to very small shearing forces, whereas with solids the deformation reaches a limit in a short time. True liquids thus show a straight line relationship between rate of shear and shearing stress, whereas complex liquids with an anomalous flow show curvilinear relationships. With the former, viscosity is independent of the pressure head, but with the latter the viscosity varies with the degree of complexity or degree of departure from a true liquid.

Mack [9] separated the asphaltenes and malthenes from a series of five asphaltic bitumens, and then, by mixing the asphaltenes from one bitumen with the malthenes from another bitumen in 10 and 15 per cent. concentration, made up a series of synthetic asphaltic bitumens. With the malthenes from one particular bitumen, it was found that true liquids were obtained with the asphaltenes from any of the bitumens; while with the malthenes from another bitumen, complex liquids showing anomalous flow were obtained with asphaltenes from any of the bitumens. The difference between the true liquids and the complex liquids was shown by determining the viscosity over a range of temperatures with a falling cylinder apparatus, with the complex liquids the velocity at which the cylinder descends was not proportional to the pressure or sheer stress but increased more rapidly than the pressure.

Mack showed that increasing the concentration of asphaltenes gave a marked increase in viscosity. The same concentration of asphaltenes gave much lower viscosities with the first type of malthenes (which always gave true liquids) than were obtained with the second type of malthenes (which gave bitumens showing anomalous flow). The apparent molecular weight of the asphaltenes is thus shown by Mack to be much higher in the latter than in the former.

Thus, asphaltenes when mixed with malthenes in which they are only partially soluble, are associated together and the particle weight is much higher than the molecular weight. Asphaltic bitumen consisting of asphaltenes dispersed in malthenes is thus largely dependent as regards its flow properties on the malthenes. Mack [9] points out that if these are rich in sulphur or aromatic in character they are good solvents for asphaltenes and

tend to give true liquids; if these are poor solvents then the asphaltenes are dispersed rather than dissolved and the individual molecules of asphaltenes are associated together to give relatively large particles. Saal and Koens [28] also found that the degree of plasticity is primarily governed by the nature of the malthenes and that the kind of asphaltenes appears to be a matter of secondary importance.

Flow Properties and Temperature.

The flow properties of asphaltic bitumen over a range of temperatures may vary widely, and it does not necessarily follow that two asphalts with similar viscosity temperature relationships at high temperatures (at which bitumen–aggregate mixtures are manufactured) will show the same relationship in viscosity or penetration at low temperatures (such as found in the road).[22, 23] Mack [9] pointed out that the change in consistency with temperature is of a complex order and that the factors which must be considered are :—

(1) Concentration of asphaltenes,
(2) Molecular weight of asphaltenes,
(3) Increase of degree of association with falling temperatures,

although the main factor is the nature of the oily constituents that is their chemical composition.

At the higher temperatures the viscosity–temperature characteristics are dependent on the character of the malthenes, but at low temperatures such factors as the degree of association of the asphaltenes and possibly the structure of the asphaltic bitumen may be more important.

Flow Properties and Structure.

It has long been known that the consistency of an asphaltic bitumen varies according to its history, that is on the previous thermal treatment or to the amount of mechanical working; this variation is obviously related to the structure of the asphaltic bitumen,[24] since no alteration has been made in the asphaltene or malthene content or composition. It has also been shown that asphaltic bitumen gradually becomes slightly harder and this age-hardening varies with different bitumens (more marked with air-blown than steam-refined or cracked) and is connected with the formation of structure since by liquefying the bitumen and re-cooling the original hardness can be regained unless too great a time has elapsed.

Oxidized asphalts when heated to temperatures which are below the cracking temperature show a reduction in consistency. Holmes and Raphael [25] found that, as shown by the consistency–temperature relationship, synthetic asphalts made by blending asphaltenes, asphaltic resins and oily constituents did not combine together in exactly the same manner as they existed in the original bitumen. This, again, is further evidence for the presence of structure in asphaltic bitumens.

It has already been seen that the asphaltenes are associated; that is, the number of individual molecules are attached to one another to form larger particles, and it may be that these large clusters of molecules become interlocked so that a structure is formed in the asphaltic bitumen. The asphaltenes according to Nellensteyn's theory are surrounded by layers of

hydrocarbons, and it may be that groups of molecules of asphaltenes are similarly surrounded by hydrocarbons so that a kind of gel structure is also present.

Such a structure in the bitumen will be destroyed by mechanical working and also by heating when the viscosity of the oily medium is reduced and the asphaltenes tend to dissolve. On cooling, the formation of these clusters of particles may take place slowly and thus afford an explanation of age-hardening : this hardening is probably most rationally explained on the gel structure outlined above due to the withdrawal of the oily medium into close association with the asphaltenes.

Visual evidence of structure in asphaltic bitumens is apparently presented when the surface is treated with suitable solvents : bitumens showing anomalous flow give designs on the surface, whereas bitumens which are essentially liquid show no patterns on the surface.[26]

Viscosity, Penetration, and Softening Point.

The flow properties of asphaltic bitumen can be determined by viscosity measurements made over a wide range of temperatures, and a number of methods have been suggested for the correlation of viscosity with penetration and softening-point determinations. Some of these introduce new arbitrary units as in the Hoepfner–Metzger method [21] which is undesirable, since such correlations should be based on absolute units.

Saal [27] in 1933 showed that it is possible to convert the penetration into absolute viscosity for non- or slightly plastic bitumens, but that this does not hold for plastic bitumens. More recently it has been shown that readings of the penetration at different depths can be used for measuring consistency and for deciding whether a bitumen is a simple or a complex liquid.[24,28]

A number of methods have been suggested for the expression of susceptibility of asphaltic bitumens (change of consistency with temperature) using penetration measurements at different temperatures and softening points. The softening point does give a measure of the temperature at which the viscosity is about the same, but it has been shown that actually the viscosity at the softening point ranges from 8/30,000 poises.[24, 27]

Methods have been put forward for the determination of flow properties at very low temperatures by Hoepfner–Metzger [29] and Fraas,[30] but such arbitrary tests do not give information which cannot readily be obtained from the determination of penetration at a series of temperatures. Holmes and co-workers [22] found it necessary to use three different factors to express the consistency temperature relationship of the range of temperatures met with in practice, and these were based on softening point, penetration at two temperatures and Saybolt Furol viscosity at 135° C. Other authors [10] have put forward other penetration–temperature relations, and viscosity indices based on viscosity–temperature changes have been proposed by other workers.[23]

Ductility.

Ductility is related to plasticity in that bitumens of marked plasticity, such as blown bitumens, have a lower ductility than bitumens which approach true liquid. Saal and Koens [21] point out that in the ductility test

the shear stress at the smallest section of the bitumen briquette is greatest and with plastic bitumens this implies a lower viscosity in these sections than in the wider sections of the briquette: this is due to the relationship already discussed in connection with the rate of shear and shearing stress. There is, therefore, less tendency for continuity of plasticity throughout the briquette to be preserved than with bitumens which are liquids and this leads to more rapid breaking and lower ductilities. In the work of Holmes and Raphael [25] it was shown that synthetic bitumens of low resin content had poor ductility (with low consistency temperature change), and synthetic bitumens of high resin content, high ductility (with high consistency temperature change).

Elasticity.

The elasticity of bitumen and bitumen–aggregates is of great importance in considering the effect of the impact of road vehicles on the road surface since if the latter is truly elastic no permanent deformation of the surface should result, as, for example, the formation of wavy surfaces usually attributed to road vehicles.

Elasticity, again, is a flow property and can be measured more readily for asphaltic bitumens at relatively low temperatures, that is at the temperatures used in practice. At such temperatures the permanent deformation (viscous or plastic) is small, and therefore the non-permanent deformation (elastic) can be detected.[32] Relatively little is known as regards the relationship of elasticity to structure, but even less is known of the structure and molecular weight of rubber which often is regarded as a typical elastic substance, than of asphaltic bitumen. Rubber exhibits the same behaviour as asphaltic bitumen in that the consistency is markedly decreased by mechanical working but increases again on standing. Comparatively little work has been done towards the evaluation of elasticity, but Saal [27] points out that the elasticity of asphaltic bitumen after bending or shearing is greater in proportion if the plasticity is more pronounced, and thus the degree of elasticity may be broadly said to be related to the degree of plasticity.

The work on consistency temperature relation does enable us to take a more rational viewpoint of the relation between penetration, softening point, ductility and elasticity, but it is obvious that this inter-relationship is only just beginning to be understood.

Colour.

Another physical property in addition to the various flow properties grouped under the heading of consistency which should be discussed is colour.

Since most hydrocarbons are relatively lightly coloured, the same will apply to colloidal solutions of such hydrocarbons. It has been stated by Nellensteyn that the dark colour of asphaltic bitumen indicates the presence of free carbon. Asphaltic bitumens of light colour (and accordingly low asphaltene content) are finding more extensive use both in building and in road surfacing: in building work the principal application appears to be the production of coloured roofing and flooring materials and for road purposes the laying of coloured rolled asphalt.[33] It is found that with such light coloured binders it is possible by admixture with aggregates of light colour

or with pigments such as natural iron oxides to make variations in the colour of the surface from the black colour normally associated with bituminous binders. The production of light coloured surfaces more particularly for night-driving is also important although in this case, factors other than the colour of the asphalt have to be considered, such as the diffusion of light from street lighting or oncoming traffic by the road surface.

Chemical Properties—Changes Produced by Light and Oxidation.

The durability of the paving surface is dependent not only on the flow properties of asphaltic bitumen and bitumen–aggregate mixtures, but also on the degree of resistance to weathering.

Chemical properties, changes produced by weathering, refer to the formation of new chemical compounds and thus include both polymerization and oxidation. The effect of oxygen on asphaltic bitumen at high temperatures is primarily one of polymerization rather than the formation of compounds containing oxygen. Dehydrogenation also takes place as shown by formation of water.

Alteration by light and oxidation occurs with the asphaltic bitumen itself, but in weathering in the presence of water the bitumen–aggregate mixture must also be considered. The contrast between coal tar [34] and bitumen in respect of change of characteristics on exposure is so marked that it might be assumed that changes in asphaltic bitumen over a period of time could be neglected; however, asphaltic bitumen extracted from road surfaces after a period of years is found to have undergone hardening. Undoubtedly the hardening of bitumens which occurs during mixing with the aggregate accounts for much of the increase in hardness found in the road surface. Hubbard and Gollomb [35] stated that in normal plant practice, as shown by the record of eight plants, an average drop of 12–14 points in penetration was found by paving asphalts of 50 and 60 penetration.

Reference has already been made to the age-hardening of bitumen, and this may be the cause of the deterioration of some surfacing mixtures which are satisfactory with light traffic and fail under heavy traffic, since the effect of the traffic in working the bitumen is to prevent the building up of a structure leading to the hardening of the bitumen. Whilst asphaltic bitumen in the mass undergoes relatively little change at atmospheric temperatures over long periods of time, changes do take place when it is in the form of thin film; Hubbard and Reeve [36] in 1913 found that in a period of twelve months asphaltic bitumen of 228 penetration in thin films hardened to 55 penetration and at the same time the weight increased by about 0·9 per cent. The rapidity of hardening is a function of film thickness, temperature and time, and in a recent paper [35] Hubbard and Gollomb confirmed that where the penetration of bitumen recovered from asphalt paving surfaces was below 20, bad cracking occurred.

The bitumen in open texture pavements, so often constructed at the present time, will harden by continual contact with the air to a very much greater extent than that in dense pavements or pavements protected with an impermeable surface coat.

Thurston [37] made a series of synthetic asphaltic bitumens by blending asphaltenes, asphaltic resins and oils derived from a series of bitumens of

200° F. melting point from different crudes prepared either by steam-reducing or by air-blowing. He found that increased proportions of asphaltic resins improved the resistance to weathering in a laboratory exposure test, whereas increased proportions of asphaltenes or oils reduced the resistance to weathering. Asphaltenes produced by oxidation appear to be superior to those naturally present in asphaltic crudes. It is, however, difficult to correlate tests with high melting point bitumens with paving bitumens, since crudes which give excellent paving bitumens also give high melting point blown bitumens which do not resist this type of weathering test. Further, although weathering tests involving exposure of the surface to special laboratory light sources have been used for a long period of time, it cannot be said that they correlate satisfactorily with practice.

In summarizing the effect of weathering on asphaltic bitumen it should be noted that the effect of overheating asphaltic bitumens, such as frequently occurs in the mixing of bitumen and aggregate, is largely due to evaporation of the lighter constituents giving harder bitumens, although alteration of the asphaltenes may occur producing more insoluble bodies and even "carbon"; the permanent hardening which occurs at ordinary temperatures may also be due to evaporation, although the work cited (Hubbard [31]) shows that oxidation also occurs. It was also shown that there was a considerable increase in asphaltenes even where allowance had been made for the loss by volatilization. Thurston and Knowles [13] showed that asphaltenes are more readily oxidized than the asphaltic resins and oily constituents giving the even more insoluble carboids. Carbon tetrachloride solutions on exposure to light are known to form precipitates presumably carboids, and, indeed, this property of the formation of insoluble material by light from asphalt was used for the production of the earliest photographs. The normal change due to weathering, apart from evaporation, appears to be polymerization, although oxidation does occur to some extent. Asphaltenes, isolated from the bitumen, were found to be readily oxidized [13] and the carboids produced apparently contained organic esters; however, even at high temperatures the action of oxygen appears to be mainly polymerization rather than oxidation, and no carbenes are present in air-blown bitumens carefully manufactured. Thus in bitumens the presence of oily constituents protects the asphaltenes from oxidation.

With open texture pavements in particular, but also with all pavements, the alteration of bitumen–aggregate mixture in contact with water, especially at low temperatures, is very important. This subject involves adhesiveness of the bitumen to road aggregates and has been very extensively studied in recent years. Nicholson [38] in 1932 applied the work of Bartell to the phenomenon of adhesion tension of asphalt pavements, and developed a test in which coarse sand coated with asphaltic bitumen was shaken with water either at room temperature or at 140° F. for one hour, after which the amount of sand from which the bitumen had been removed was noted. He found a marked difference in adhesion tension between different types of mineral materials, classifying silica amongst the fillers that like water better than bitumen, and limestone dust amongst those liking bitumen better than water. The work of Riedel and Weber [39] is well known, in which the adhesion of the asphaltic bitumen to mineral aggregates is measured by placing the coated aggregate in contact with boiling water or

with sodium carbonate solution. Other investigators, however, do not consider this test satisfactory and point out that the experimental conditions cannot be considered to duplicate road practice, first as regards temperature and secondly as regards the use of sodium carbonate solution, and much experimental work has shown that the method may give misleading results.[40, 43] A. R. Lee [41] showed that there is very little difference with the various types of stone commonly used in road construction, in wetting properties towards bitumen, when the stone surface is highly polished and previously wet with water; there appears to be little basis for the suggestion that acidic stones give poorer adhesion than basic stones towards various binders owing to their so-called acidic or basic character. The binder was shown to have much more difficulty in wetting rough stone surfaces which are already in contact with water than in wetting smooth surfaces, and thus differences due to various degrees of roughness are much greater than any differences due to the nature of the material. Hermann [42] is in agreement with this conclusion, but points out that in addition to surface moisture, surface roughness and porosity attention must be paid to the surface dust on the stone. B. H. Knight [43] has also provided strong support for the importance of surface texture and grain size of the constituent minerals in the aggregate, and he also states that adherent coating such as limonite improves adhesion. Some early work, however, in which bitumen solutions were decolorized to different extents with different aggregates show that surface texture is not the only explanation.

The adhesiveness of bitumen to aggregate is probably of little importance in influencing retention of the stone with traffic which is primarily dependent on viscosity of the bitumen. It is, however, of importance when deterioration of the road surface has begun, and examination of the small pieces of stone thrown by traffic to the side of a road which is failing will often show that these are only partly covered by bitumen although initially they were completely covered. It appears that adhesiveness of bitumen to aggregate is determined by the following, arranged in probable order of importance :—

(1) Flow properties of the bitumen,
(2) Surface texture of the stone,
(3) Chemical composition of the surface of the aggregate (not necessarily of the stone itself),
(4) Chemical composition of the bitumen,

and thus both physical and chemical properties of the asphaltic bitumen are involved.

In summarizing the work reviewed in this paper the lack of a number of connecting links in our present knowledge is evident. The selection of bitumens for road use in time past has been largely on the basis of comparison with bitumens of known experience, and a number of irrelevant tests and properties based on such comparisons have been put forward as criteria, such as sulphur content, paraffin wax content, or even the spot test of Oliensis, although these may have no relation to flow properties or resistance to change which should be the deciding factors.

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REFINING OF SHALE OIL IN SCOTLAND.*

By G. H. Smith,† Ph.D. (Member), and W. B. Peutherer,† F.I.C. (Member).

Summary.

Refining of shale oil in Scotland has been directed at different periods to the production of various primary products. In the early days of the industry burning oil was the main objective of the refiner, but as the industry developed, the refining of shale oil aimed at the production of a full range of products—motor spirit, solvent naphtha, burning oil, gas oil, wax, light lubricating oil and fuel oil. Such processes have been adequately described in previous publications, and this paper deals with what are to-day the most important products—diesel oil for high-speed compression-ignition engines, motor spirit and wax.

The chemistry of shale oil—particularly Scottish shale oil—is briefly reviewed, but unfortunately only the lightest fractions have been studied to any great extent.

The various refining steps to produce the maximum quantity of diesel oil are indicated, together with the experimental work on which the present refining scheme is based.

Wax extraction and refining, which at the moment is a necessary feature of any such refining scheme, is dealt with in some detail.

Alternative methods for the manufacture of motor spirit from shale oil, with special reference to their effect on octane rating, are discussed.

I. Chemistry of Shale Oil.

Shale oil is a decomposition product of the organic matter in oil shale, but up to the present it has been found impossible to isolate this material. The obvious method of extraction by solvents has proved only partly successful. Gavin and Adyelotte [1] reported the extraction from certain shales by organic solvents of 10·98 per cent. or 55·8 per cent. of the yield of oil by distillation. Hentze,[2] on the other hand, attacked Kukersite with the inorganic acids, hydrochloric and hydrofluoric, and then extracted the residue with chloroform, whereby he isolated 72 per cent. of the bitumen in the shale. Bailey [3] obtained a yield of 0·98 per cent. of organic matter (10 per cent. of the distillation yield of oil) by extracting Scotch shale with carbon disulphide and chloroform for 12 days.

By distillation under reduced pressure, McKee and Goodwin [4] obtained from certain shales an intermediate product between the bitumen as it exists in shale and shale oil. This material was highly unsaturated, being completely soluble in sulphuric acid (sp. gr. 1·84). On distillation, decomposition took place, giving oil, 48 per cent. insoluble in acid, and coke. Distillation apparently breaks down the heavy polymers into more saturated hydrocarbons and coke.

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† Scottish Oils, Ltd.

The nature of shale oil, therefore, depends first on the fundamental nature of the organic material, and secondly on the method and rate of retorting.

Shale oils, like petroleum, can be generally classified as paraffin, mixed or asphaltic base, although all contain a considerable proportion of unsaturated hydrocarbons. Scotch, Australian and Fushun (Manchuria) shale oils are examples of the paraffin crudes, whilst Estonian and Tasmanian shale oils fall into the asphaltic class. The spirit fractions of the latter are characterized by the comparatively high aromatic content (13–15 per cent.), whilst the former contain only traces of aromatic compounds.

Hydrocarbons.

As regards the hydrocarbon content of Scotch shale oil, little information is available outside the motor-spirit range. An analysis of shale spirit gives the following composition :—

Paraffins	42·5%
Naphthenes	9·5%
Unsaturated hydrocarbons . . .	48·0%

Steuart [5] isolated pentane and *iso*pentane, hexanes and heptanes, and identified the naphthenes, methyltetramethylene, pentamethylene, hexamethylene and methylhexamethylene.

Sulphur.

The sulphur content of Scotch shale oil is low (0·45 per cent.) and its distribution is shown in Table I.

TABLE I.

Distillation at 11 mm. Hg.

	Temp., ° C.	Sp. Gr.	Sulphur, %.
Fraction 0–20	46·5–128	0·8057	0·211
,, 20–40	128 –182·5	0·8522	0·297
,, 40–60	182·5–235	0·8777	0·307
,, 60–80	235 –285	0·8979	0·311
,, 80–90	285 –320	0·9101	0·348

The sulphur compounds present in the light fractions of Scotch shale oil are mercaptans, thioethers and thiophenes. Carbon disulphide is absent. No information is available as to the composition of the higher-boiling sulphur compounds. The extent to which the sulphur compounds in shale oil decomposed on heating is illustrated in Table II and Fig. 1. The

TABLE II.

Temp., ° F.	H_2S Formed, gms./100 ml. of oil.
300	0·0068
400	0·0082
500	0·0085
600	0·0167
700	0·0198
750	0·0400
800	0·0756

crude oil was heated in an autoclave for 4 hours at temperatures ranging from 300 to 800° F., and the H_2S formed was determined.

At 500° F. the decomposition of the sulphur compounds becomes very rapid, until at 800° F. almost 20 per cent. of total sulphur in the oil is converted to hydrogen sulphide.

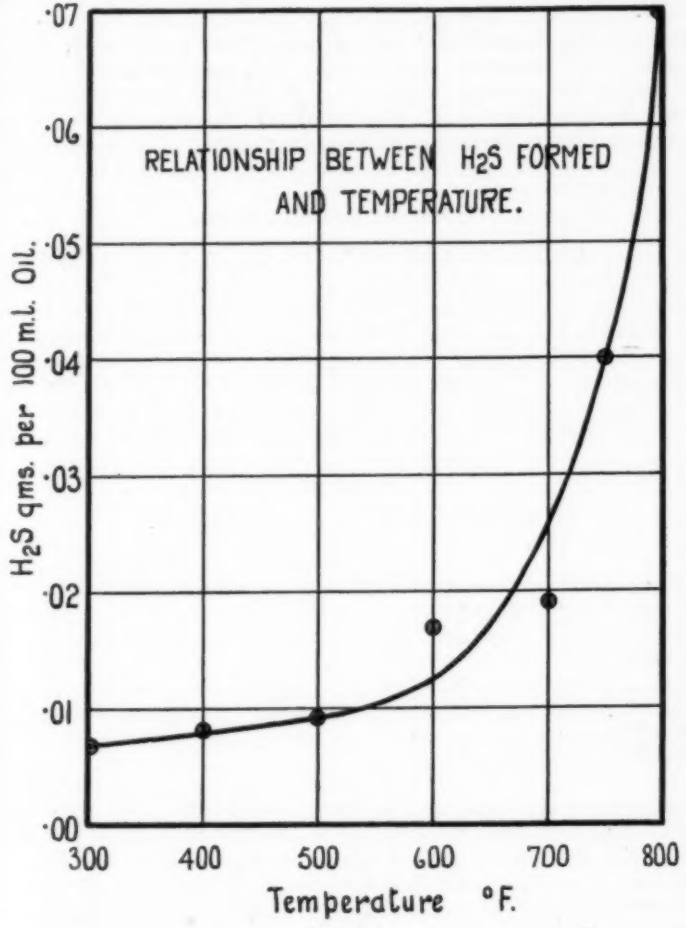


FIG. 1.

Nitrogen.

Nitrogen is present in the shale oil to the extent of 0·75 to 1 per cent. and exists mainly as basic compounds such as pyridine and its derivatives.

Robinson [6] and Robinson and Goodwin [7] identified the following bases of the leucoline series: $C_{12}H_{13}N$, $C_{13}H_{15}N$, $C_{14}H_{17}N$, $C_{16}H_{21}N$, whilst Garret and Smythe [8] isolated and identified pyridine, 2-methylpyridine,

2 : 6-dimethylpyridine, 2 : 4-dimethylpyridine, 2 : 5-dimethylpyridine, and 2 : 4 : 6-trimethylpyridine. Beilby [9] showed that of the total nitrogen present in the oil shale only 20–25 per cent. appears in the oil. On distilling the crude oil to coke, 50 per cent. of the nitrogen is lost as ammonia.

Phenols.

The phenol content of Scotch shale oil varies from 2 to 4 per cent. Gray [10] separated and identified phenol, *ortho*cresol, *meta*-cresol and xylenols, and showed the presence of guaiacol. Crude spirit from cracking shale oil contains about 1 per cent. of phenols, of which have been isolated cresols, xylenols and higher phenols, xylenols predominating.

II. Refining of Shale Oil.

It is possible to produce from Scotch shale oil a whole range of products—spirit, kerosene, gas oil, light lubricating oil, diesel oil, wax, fuel oil and coke. This process of "full refining" has been adequately described by Bailey,[3] and by Smith, Allen and Grant,[11] and while modern equipment and refining technique would probably alter the application of the methods described by these authors, the basic principles would be substantially the same. It is proposed to deal here with the manufacture of what are to-day the most important products of the shale industry—diesel oil and motor spirit,

Table III.

Analyses of Shale Oil and Scrubber Naphtha.

	Crude Oil.		Scrubber Naphtha.
Carbon	85·83%		—
Hydrogen	12·64%		—
Nitrogen	0·74%		—
Oxygen (by diff.)	0·33%		—
Sulphur	0·46%		—
Chlorine	Nil		—
Sp. gr.	0·877		0·736
Flash point	140° F.		—
Setting point	85 ,,		—
	Engler Dist.	Dist. at 10 mm. Hg.	Engler Dist.
I.B.P.	160° C.	48° C.	48° C.
10% dist. at	222 ,,	97 ,,	78 ,,
20% ,,	256 ,,	128 ,,	87 ,,
30% ,,	285 ,,	159 ,,	95 ,,
40% ,,	314 ,,	183 ,,	102 ,,
50% ,,	338 ,,	207 ,,	110 ,,
60% ,,	355 ,,	232 ,,	118 ,,
70% ,,	369 ,,	256 ,,	129 ,,
80% ,,	379 ,,	283 ,,	146 ,,
90% ,,	384 ,,	323 ,,	172 ,,
F.B.P.	384 ,,	346 ,,	245 ,,
Total distillate	96·5%	96·0%	98·0%
Residue	3·0%	2·5%	1·0%
Loss	0·5%	1·5%	1·0%

the term diesel oil being limited to fuel suitable for the modern high-speed compression-ignition engine. Two distinct processes are described: refining to (1) maximum diesel oil, which necessarily includes wax extraction and refining, and (2) maximum motor spirit. Shale oil from the present retorts is collected in two portions: (1) crude oil from the condensing system, and (2) "scrubber naphtha," the light spirit extracted from incondensable gas, and these two products are processed separately in the refinery.

Manufacture of Diesel Oil.

Scotch shale oil is an ideal base for diesel oil, and yields on appropriate treatment 40 to 50 per cent. of first-grade light diesel oil.

Alternative refining reagents which have been considered are sulphuric acid and liquid SO_2. Whilst there are possibilities of using the above reagents in one particular refining scheme, each in its most useful sphere, they are dealt with separately here.

Refining by Sulphuric Acid (sp. gr. 1·84).

In refining with sulphuric acid the main operations are:—

(*a*) Distillation to coke.
(*b*) Extraction of wax from press cut.
(*c*) Acid and soda treatment of wax-free oil.
(*d*) Re-running treated diesel oil.
(*e*) Pressure distillation of the residue from (*d*).

(*a*) *Distillation to Coke.*

The carbon/hydrogen ratio of shale oil is higher than that of the average petroleum, and at the same time the oil is more unstable, so that a distillation to coke effects a mild cracking, yielding a distillate more saturated than the crude oil. This distillation, therefore, is a definite step in refining as well as a means of fractionating the crude. Consideration has been given as to whether distillation under vacuum or under normal pressure would be most advantageous, and a few of the major points brought out during this inquiry are given below.

The work was carried out in a 5-gallon still with a short fractionating column at pressures varying from 15 mm. Hg to normal pressure. In all cases the distillate was cut to spirit, wax-free cut, pressible cut and residue. A 10 per cent. residue was found to contain all the amorphous wax, and was then distilled to coke at atmospheric pressure under mild cracking conditions, producing a distillate containing crystalline wax, which was added to the pressible cut. The pressible cut was dewaxed and blended with the wax-free cut, and the blend treated with sulphuric acid and caustic soda and re-run to diesel oil. All treatments were identical, to give a true comparison, and diesel oil was refined to the same volatility in each case. The yields of three typical tests and essential characteristics of the diesel oil are given below:—

TABLE IV.

Diesel Oil.	Distillation Pressure.		
	15 mm. Hg.	330 mm. Hg.	Atmospheric.
Loss on treatment, % on crude . . .	10·6	10·6	10·0
Yield, % on crude	53·5	59·9	61·3
Aniline point, ° C.	55	57	58
Carbon residue (Conradson), % . . .	0·10	0·03	0·008
Viscosity (Redwood No. 1) at 100° F., secs..	38	35	35

Distillation at atmospheric pressure therefore gives not only a higher yield of diesel oil, but also a better diesel oil, as indicated by the higher aniline point and lower carbon residue. The effect of the distillation at atmospheric pressure is to decompose unsaturated polymers which are to a certain extent preserved in vacuum distillation.

In the refinery the distillation of the crude oil to a 15 per cent. residue is effected in a pipe-still and bubble-tower unit of conventional design (see flow diagram, Fig. 2). The products taken are :—

TABLE V.

Overhead	Crude spirit	6%	Sp. gr. 0·778
Tray cut	Wax-free cut	23%	,, 0·816
,, ...	Pressible cut	56%	,, 0·890
Residue		15%	,, 0·960

The feed temperature necessary to run to a 15 per cent. residue is 750–760° F. when operating at 1 lb. of steam per gallon of distillate. It is possible to work to 10 per cent. residue, but the free carbon content of the residue, due to increased decomposition of the oil, is rather high, whereby the lower trays of the fractionating column are liable to be fouled. The residue contains all the amorphous wax cut which is in the fraction 10–2 per cent. on crude. By coking this residue under mild cracking conditions, the amorphous wax is rendered crystalline and at the same time the residue is partly cracked to lighter oils. The distillate from the coking stills is thereafter recycled as feed to the crude unit. The products from this distillation and coking are : spirit, wax-free cut, pressible cut and coke.

The coking operation is carried out batch-wise in pot stills. The coke is valuable on account of its low volatility (5–7 per cent.) and ash content (less than 0·5 per cent.) for making carbon electrodes for the aluminium industry. In some cases a coke of even lower volatility is required, but it is impossible to produce this in the conventional coking stills. The volatile matter content can be reduced to 1 per cent. by processing the coke through an ordinary Scotch shale retort operating at coke temperatures of 1400° F. The optimum throughput is 3 tons per retort per day, and is best carried out in a current of steam. Under these conditions the loss is 12 per cent. To reduce the volatile matter still further, some type of calciner with direct heating is necessary, such as that described by Watkins.[12]

CRUDE OIL DISTILLATION UNIT.
VAPOUR
FRACTIONATING COLUMN
STEAM
PIPE STILL
REBOILER PUMP
CONDENSER
SEPARATOR
REFLUX TANK
REFLUX PUMP
RESIDUE TO COKING STILLS
HEAT EXCHANGERS
FEED PUMP
COOLER
COOLER
CRUDE OIL
WAX FREE CUT
PRESSIBLE CUT
SPIRIT

FIG. 2.

Below are given analyses of the normal production of shale coke (5–7 per cent. volatile matter) and coke of volatile matter 1 per cent.

TABLE VI.

	Normal Shale Oil Coke.	Low Volatility Shale Oil Coke.
Moisture	1·84%	1·92%
Volatile matter (less moisture)	5·28%	1·00%
Fixed carbon	92·50%	96·64%
Ash	0·38%	0·44%
Carbon	92·50%	94·60%
Hydrogen	2·40%	0·60%
Sulphur	0·38%	0·40%
Calorific value (B.Th.U./lb. (gross)	14,800	13,980

(*b*) *Extraction of Wax from Press Cut.*

The pressible cut itself is of too high viscosity to ensure satisfactory filtration, and is blended back with wax-free cut to a viscosity of 50 secs. (Redwood No. 1) at 100° F. The wax is extracted in two stages, leaving a dewaxed oil, setting point 22° F. The extraction and refining of the paraffin wax are dealt with in a separate section later.

(*c*) *Acid and Soda Treatment of Wax-free Oil.*

The dewaxed oil blended with the wax-free cut and spirit still residue is termed "Crude Diesel Oil," and is subjected to treatment with sulphuric acid, sp. gr. 1·84, and caustic soda, 10 per cent. solution.

The possible variations in acid treatment are :—

(i) Divided treatment—*i.e.*, treatment in various fractions, giving each fraction the appropriate treatment as against treatment of the diesel oil as a whole.
(ii) Percentage treatment.
(iii) Temperature of treatment.

(i) *Divided Treatment.*

The crude shale oil was cut into four fractions, viz. 0–20 per cent., 20–30 per cent., 30–55 per cent., and 55–90 per cent. each fraction (after

TABLE VII.

Fraction.	% on Crude.	Sulphuric Acid Treatment, % on fraction.	Loss on Acid and Soda Treatment, % on fraction.	Treated Oil, % on crude.
0–20·2%	20·2	2·0	6·8	18·8
20·2–30%	9·8	2·0	9·8	8·8
30–55·1% (after dewaxing)	23·8	3·0	16·5	19·9
55·1–93·7% (after dewaxing)	33·6	3·0	18·5	27·4
Totals for divided treatment	87·4			74·9
Blend of all fractions	87·4	2·5	13·4	75·7

dewaxing the cuts containing wax) given the necessary treatments to give satisfactory diesel oils, and the results were compared with a straightforward treatment of the blended distillates. Below are given details of yields, and these figures show that no advantage is to be derived from treating the oil in separate fractions as compared with treating the oil as a whole.

(ii) *Percentage Treatment.*

Two series of tests were made: one in which acid alone was used, and the other where, before acid treatment, the oil was subjected to tar from a previous treatment. Results are given in Table VIII.

TABLE VIII.

Treatment Temperature, 65° F.

	Acid Alone.			Tar and Acid.		
Sulphuric acid, % by volume .	3·5	3·0	2·5	2·5	2·0	1·5
Finished Diesel Oil.						
Colour, ¼-in. cell, Lovibond, 510 and 200 series	5·2Y 0·2R	5·0Y 0·4R	6·0Y 0·35R	5·2Y 0·1R	6·5Y 0·4R	15Y 0·85R
Stability test	Stable.	Stable.	Failed.	Stable.	Stable.	Stable.

The use of tar from a previous treatment shows a definite saving in acid. With acid alone 3 per cent. is necessary, but with tar only 2 per cent. is required to give the same product.

(iii) *Temperature of Treatment.*

The temperature range explored was 45–100° F. and the treatment in all cases was 3 per cent. of acid by volume. From Table IX., which shows the effect of increasing the temperature, it is concluded that the optimum temperature as regards colour is 65° F. It is noteworthy that the treatment at the highest temperature, 100° F., does not result in a greater loss than that at 65° F., and in actual practice the higher temperature is preferred, owing to the greater fluidity of the tar.

TABLE IX.

Sulphuric Acid Treatment—3% by Volume.

Initial Temperature of Treatment.	45° F.	65° F.	80° F.	100° F.
Loss on treatment, % by vol. .	13·2	15·1	14·6	14·8
Finished Diesel Oil.				
Colour, ¼-in. cell	9·5Y 0·55R	5·0Y 0·4R	5·0Y 0·4R	6·0Y 0·3R
Stability test	Failed.	Stable.	Stable.	Stable.

(*d*) *Re-running of Treated Diesel Oil.*

The treated diesel oil shows only 75–80 per cent. distilling to 350° C., and in addition certain polymerized products are formed during the acid treatment, so that the treated oil has necessarily to be re-run.

The question as to whether vacuum distillation or atmospheric distillation of this oil would be most advantageous was the subject of a separate inquiry, and the results showed that the diesel oil from vacuum distillation was slightly better in colour. Whilst this was not apparent in an oil of volatility 95 per cent. at 350° C., it was appreciable if the diesel oil was run to a high end-point such as 80 per cent. at 350° C., but the advantages of vacuum distillation were so small as to be disregarded.

Re-running is normally effected in a pipe-still and bubble-tower unit with steam at 1 lb. per gallon. A spirit cut is taken as overhead, diesel oil as tray cut, leaving a residue of 20 per cent.

(*e*) *Pressure Distillation of Residues.*

This 20 per cent. residue is still a potential source of diesel oil, and can be converted into diesel oil and spirit by pressure distillation at 50–75 lb. per sq. in. and 780–790° F., yielding approximately 30 per cent. of finished spirit, 40 per cent. finished diesel oil, pitch 15 per cent., gas and loss 15 per cent. The diesel oil from cracking this material, unlike cracked gas oil from petroleum, which shows considerably lower aniline point than straight-run gas oil from the same source, is of approximately the same aniline point as diesel oil from the straight distillation of the shale crude—*i.e.*, aniline point 63° C. The diesel oil thus produced requires less acid to refine, and the losses are correspondingly lower.

Another potential source of diesel oil is wax. On pressure distillation, 50 lb. per sq. in., the wax yields spirit 35 per cent. diesel oil 45 per cent. coke and gas 20 per cent. The diesel oil fraction, however, whilst of high aniline point (76° C.) is of very low specific gravity (0·785) and viscosity (34 secs. at 70° F.), which at the moment are considered disadvantages. As expected, the spirit produced is of poor engine test (Octane No. 39), and to get this to anything like a commercial octane rating would mean a very high loss in reforming.

Refining Scheme.

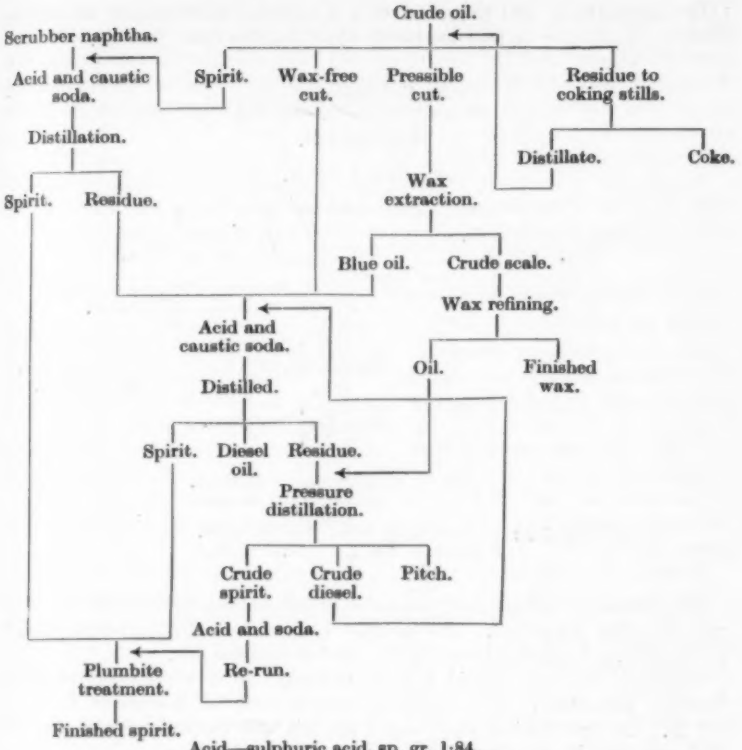
A typical scheme for the production of diesel oil from shale oil with sulphuric refining acid is given on opposite page.

Properties of Shale Diesel Oil.

Shale diesel oil manufactured by refining with sulphuric acid and caustic soda has the following characteristics. (Table X).

Refining by SO_2 Treatment.

The natural alternative to sulphuric-acid refining is extraction by liquid SO_2. This has been applied experimentally to crude shale-oil distillate both before and after dewaxing. The treatment of the wax-bearing distillate offered several advantages, the principal of which was the production of a crystalline and cleaner wax, but, on the other hand, the treatment has to be carried out in two stages : one at a comparatively



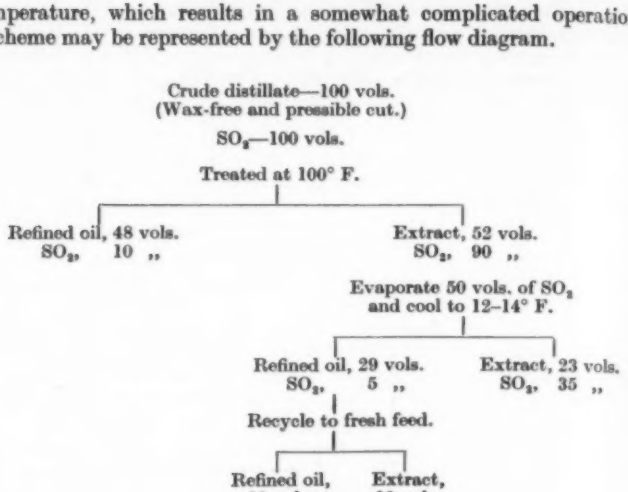
Acid—sulphuric acid, sp. gr. 1·84.
Caustic soda—10 per cent. solution.

TABLE X.

Analysis.

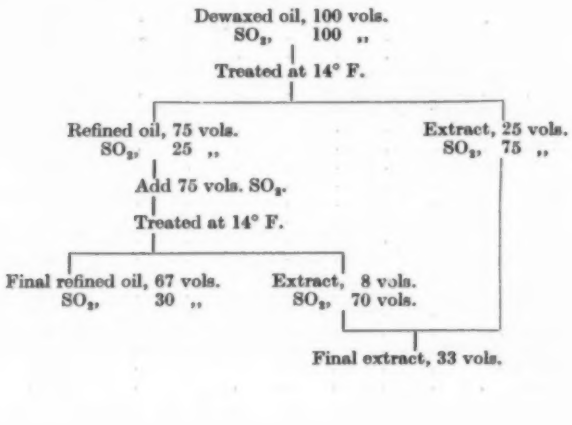
Sp. gr	0·841
Aniline point	64° C.
Sulphur	0·32%
Carbon residue (Conradson)	Nil.
Cal. val., B.Th.U./lb. (gross)	19,530
Setting point (I.P.T.)	12° F.
Cetene number	72
I.B.P.	209° C.
10% dist. at	233 ,,
20% ,,	244 ,,
30% ,,	258 ,,
40% ,,	270 ,,
50% ,,	284 ,,
60% ,,	300 ,,
70% ,,	316 ,,
80% ,,	330 ,,
90% ,,	350 ,,
F.B.P.	374 ,,
Total distillate	98·5%
Residue	1·0%
Loss	0·5%

high temperature, which results in a somewhat complicated operation. Such a scheme may be represented by the following flow diagram.


Crude distillate—100 vols.
(Wax-free and pressible cut.)
SO_2—100 vols.
Treated at 100° F.
Refined oil, 48 vols.
SO_2, 10 ,,
Extract, 52 vols.
SO_2, 90 ,,
Evaporate 50 vols. of SO_2 and cool to 12–14° F.
Refined oil, 29 vols.
SO_2, 5 ,,
Extract, 23 vols.
SO_2, 35 ,,
Recycle to fresh feed.
Refined oil, 19 vols.
Extract, 10 vols.
Final yields : Refined oil, 67 vols. Sp. gr. 0·810.
Extract, 33 ,, ,, 1·02.

The refined oil is dewaxed, given a light sulphuric acid treatment, and re-run to yield diesel oil. The extract is a non-waxy, low-setting-point, viscous oil, suitable for blending into fuel or furnace oils.

The application of liquid SO_2 to dewaxed oil is a perfectly straightforward procedure. The optimum temperature of treatment is about 14° F. In one typical experiment the oil was treated with liquid SO_2 (200 per cent. by vol.) in Edeleanu's experimental apparatus in two stages, with the results shown below. A two-stage treatment of kerosene in this apparatus corresponds to the normal countercurrent treatment of this oil in the commercial unit.



The diesel oil obtained from the refined oil by neutralizing with caustic soda and distilling was not to specification as regards colour, and a light acid treatment (½ per cent. of 96 per cent. acid followed with caustic soda) was necessary before distillation. Table XI. gives particulars of crude dewaxed oil, extract and finished diesel oil.

TABLE XI.

	Dewaxed Oil before SO_2 Treatment.	Refined Oil.	Extract.	Finished Diesel Oil.
C	85·98%	—	86·32%	—
H	12·23%	—	9·70%	—
N	0·50%	—	1·22%	—
S	0·34%	0·18%	0·94%	0·14%
O (by diff.)	0·95%	—	1·82%	—
Sp. gr.	0·878	0·829	0·988	0·817
Flash point	145° F.	179° F.	185° F.	171° F.
Viscosity (Redwood No. 1):				
At 70° F.	51 secs.	44 secs.	152 secs.	38 secs.
,, 100 ,,	42 ,,	38 ,,	70 ,,	35 ,,
Aniline point	57·4° C.	80·4° C.	Less than 0	78° C.
Setting point	20° F.	28·5° F.	,,	22° F.
Carbon residue	0·27%	0·06%	2·04%	Nil.
Bromine value	14	19	10	—
Hard asphalt	0·03%	Nil.	0·06%	—
Cal. val. (B.Th.U./lb. gross)	19,010	19,710	17,660	19,920
Colour (½-in. cell)	—	—	—	5·5Y + 0·3R
I.B.P.	192° C.	199° C.	190° C.	199° C.
10% dist. at	233 ,,	232 ,,	233 ,,	228 ,,
20% ,,	255 ,,	253 ,,	260 ,,	245½ ,,
30% ,,	275 ,,	274 ,,	288 ,,	261 ,,
40% ,,	296 ,,	294 ,,	308 ,,	275 ,,
50% ,,	314 ,,	310 ,,	326 ,,	290½ ,,
60% ,,	331 ,,	327 ,,	340 ,,	303 ,,
70% ,,	—	344 ,,	—	316 ,,
80% ,,	—	—	—	331 ,,
90% ,,	—	—	—	350 ,,
F.B.P.	>350 ,,	>350 ,,	>350 ,,	>350 ,,
Total distillate	70·0%	75·0%	64·0%	92·0%
Residue	30·0%	25·0%	36·0%	7·5%
Loss	Nil.	Nil.	Nil.	0·5%
% dist. at 200° C.	—	—	1·5	—
,, 300 ,,	42·5	43·5	36·0	58·0
,, 350 ,,	69·0	73·0	63·0	90·0

The extract as such was only of fuel value, and two methods of dealing with it have been investigated—viz., (1) cracking to spirit, and (2) hydrogenating to diesel oil.

(1) It is possible to crack the extract to spirit, but the spirit yields are low. In one series of tests in the laboratory autoclave, cracking to coke, the extract gave :—

Spirit	30%
Coke	45%
Loss and gas	25%

The crude spirit, after refining with sulphuric acid and caustic soda and re-running to F.B.P. 200° C., was of specific gravity 0·783 and Octane No. 59, which is only slightly higher than normal cracked spirit from shale

oil. The sulphur content of the spirit was high, and difficulties were encountered in refining the oil to a suitable colour and stability. The loss on treatment amounted to 7·5 per cent.

(2) The possibility of hydrogenating the extract to give diesel oil seemed practicable, but so far, while the yields—as would be expected—have been good, the cetene value of the oil is low.

The extract, therefore, has proved to be of fuel value only, and at the present time sulphuric-acid treatment, including the recovery of the residual acid which is used for the manufacture of sulphate of ammonia, is the more attractive. Special burners have been designed to deal with the washed and neutralized acid tar, so that the material extracted by the acid is still available as works fuel, the calorific value being 15,500 B.Th.U. per lb.

III. Wax Extraction and Refining.

In any method of refining shale oil to diesel oil, the other products incidentally produced are motor spirit, wax and fuel oil. The motor spirit is derived from three sources: (1) spirit extracted from the retort gases by absorption with gas oil, (2) spirit in crude oil, and (3) spirit produced by cracking the residue distilling above the diesel-oil range. The refining of this spirit is dealt with later when refining to maximum spirit is discussed.

The extraction and refining of wax may be conveniently divided into the following sections:—

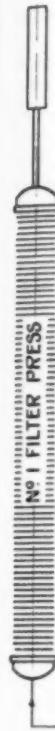
(*a*) Extraction.
(*b*) Treatment.
(*c*) Sweating.
(*d*) Decolorizing.
(*e*) Finished Waxes.

(*a*) *Extraction.*

The pressible fraction, of specific gravity 0·880 at 60° F., setting point 80° F., viscosity 50 secs. at 100° F. and containing 18 per cent. wax, is cooled and filtered in two stages, the scales obtained being refined separately.

The pressible cut is first cooled to 40° F. and the wax which separates filtered off. The blue oil is then cooled to 22–23° F. and again filtered. The first filtration is carried out at 40° F., because at that temperature a scale is obtained which, when sweated to the highest-melting-point wax prepared, gives a wax of the desired oil content. Under these conditions also, the second scale is suitable for the preparation of low-melting-point waxes. The temperature of 22–23° F. for the second filtration was chosen to give a blue oil which, when blended with the wax-free cut and redistilled, gives the necessary setting point and cloud point in the finished diesel oil. If the temperature of the second cooling is allowed to fall two or three degrees below that given, a considerable increase in the oil content of the scale is noticed.

The plant used for dewaxing at each stage consists of a heat exchanger, two coolers and two filters, with the necessary pumps and ammonia compressors. In the heat exchanger the oil is cooled by means of cold filtered oil, and in the coolers the cooling medium is liquid ammonia. These



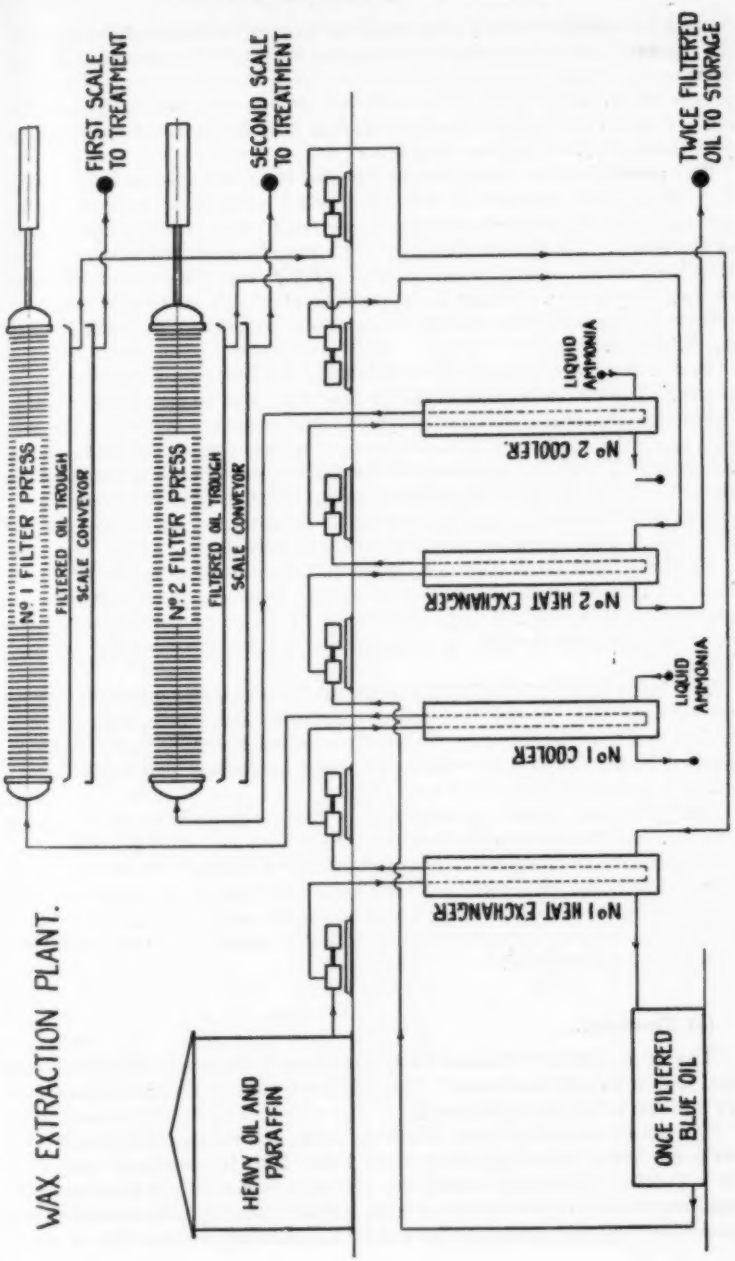

WAX EXTRACTION PLANT.
No 1 FILTER PRESS
FILTERED OIL TROUGH
SCALE CONVEYOR
No 2 FILTER PRESS
FILTERED OIL TROUGH
SCALE CONVEYOR
FIRST SCALE TO TREATMENT
SECOND SCALE TO TREATMENT
TWICE FILTERED OIL TO STORAGE
LIQUID AMMONIA
No 2 COOLER
No 2 HEAT EXCHANGER
LIQUID AMMONIA
No 1 COOLER
No 1 HEAT EXCHANGER
HEAVY OIL AND PARAFFIN
ONCE FILTERED BLUE OIL

FIG. 3.

coolers are kept full of liquid ammonia by means of a constant-level device, the gaseous ammonia produced during the cooling being drawn off by the compressor, compressed, cooled and returned to the cooler. The filter presses are of the horizontal hydraulic-plate type with loose rings. There are 510 plates in a press, and these are 3 ft. 9 in. in diameter and the rings ½ in. thick (see flow diagram, Fig. 3).

The pressible cut is pumped through the heat exchanger and cooler into the filter. The pressure on the filter is not allowed to exceed 450 lb. per sq. in., this pressure corresponding to a pressure of 600 lb. per sq. in. at the pump. For maximum oil removal from the scale it has been proved that the pressure should be as high as possible and should be maintained as long as possible. Under the present method of operating, the rate of filtration, including time taken for cleaning, works out at 0·128 gal. per sq. ft. per hr.

One of the major drawbacks to this type of filterpress is buckling of the plates. The plates bend in different directions, and so give thick and thin cakes of scale, and sometimes empty spaces are left. When a filter is in this state, the results are unsatisfactory, the filter frequently bursts before the pumping time is complete and the thick cakes of scale contain two to three times the oil of a normal-sized cake. This trouble has been largely got over by regularly turning bent plates so that they all face in the one direction. This operation is performed once a week.

In the second-stage filtration—that is, when filtering at 22–23° F.—it is found that the rate of filtration gradually becomes slower and the scale obtained becomes sticky and oily, due to the pores of the cloths clogging up; and to overcome this, it is necessary to wash the filter by injecting hot oil.

The importance of obtaining a clean, well-fractionated press cut cannot be over-stressed, as the presence of relatively small quantities of high-boiling-point asphaltic material results in a black, sticky paste being deposited in the filters from which oil cannot be pressed and which is very difficult to remove from the filter.

Under normal operating conditions a first-stage scale of melting point 118° F. and expressible oil content 15 per cent. is obtained, whilst the second scale has a melting point of about 97° F. and oil content of 25 per cent. The total scale extracted amounts to 22 per cent. of the pressible fraction, the ratio of first scale to second scale being 3 to 1. The twice-cooled blue oil has a specific gravity of 0·890, viscosity 70 secs. at 70° F., and setting point 22° F.

(*b*) *Treatment.*

The crude scales obtained from the filter presses are dark in colour and unstable, and are treated with sulphuric acid to give as low a colour as possible before being sweated.

The scales are settled until free from water and sludge, and then treated with sulphuric acid of specific gravity 1·84. This treatment is carried out in a vertical cylindrical vessel, the agitation being by air blowing. The acid treatment is given in two stages, a small quantity first to remove any moisture, followed, after tar removal, by the bulk of the acid. The quantity

of acid necessary varies with the oil content of the scale, and normally the quantity required is about 2 per cent. for scale from first cooling and 2·5 per cent. for scale from second cooling.

In order to obtain the lowest possible colour in the treated scales, the points to be watched are: (1) quantity of acid used—insufficient acid or excess acid should be avoided; (2) the temperature during treatment should be as low as possible; (3) scale should not be left in contact with acid any longer than is necessary for settling of the acid tar.

The acid-treated scales are neutralized by agitation with 10 per cent. sodium carbonate solution, this being used in preference to caustic soda solution because considerably lower colours in the treated scales are obtained and sodium carbonate is less liable to give troublesome emulsions than caustic soda. The neutralized scales are next washed two or three times with hot water to remove traces of alkali. This water-washing is important, since scales containing alkali give trouble in the sweating process. The scale does not cool to give a hard cake, but is softer than usual, and oil removal is difficult. The effect is seen both in the strainings and in the wax left in the pans.

The average colours of treated scales are—first scale, $9Y + 1R$, and second scale, $12Y + 2R$, determined in a ½-in. cell, and since these products are not perfectly colour stable, they are stored at as low a temperature as possible and for as short a period as possible before being sweated. The loss in treatment with acid and sodium carbonate amounts to between 2 and 3 per cent.

(*c*) *Sweating.*

The treated scales are next sweated to remove oil and to divide the waxes into various grades according to melting points. The plant consists of twenty-four Henderson houses (tray type) and one Alanmor stove, the Henderson houses being of approximately 17 tons capacity and the Alanmor stove of 20 tons.

From scale of melting point 118° F. are prepared waxes ranging in melting point from 118–120° to 125–130° F., whilst waxes ranging from 100–105° to 110–115° F. are prepared from the scale of melting point 97° F. The melting point and oil content of the two scales are such that when these have been sweated to the highest-melting-point wax prepared from that grade, the oil content of the wax is at the desired figure. The lower-melting-point waxes in each case are then prepared from sweatings.

The first fraction obtained from every sweating consists of oil with wax dissolved in it, and all fractions with melting point below 90° F. are collected together. The bulk, of melting point 85° F., oil content 60 per cent., and amounting to 30 per cent. on scales charged for sweating, is transferred to cracking stock. A second fraction is collected from every sweating, and these consist of wax mixtures of various melting points and oil contents. These fractions are blended with fractions which give like melting points for the oil-free waxes contained in them, five different grades of sweatings being collected. These fractions are re-sweated separately to give different grades of waxes; the higher the melting point of the oil-free wax contained in a fraction, the higher the melting point of the wax prepared from it,

care being taken in every case that there is a sufficient gap between the melting point of the oil-free wax in the fraction and the melting point of wax to which it has to be sweated, to ensure that the sweating will be of such a duration that when the melting point desired in the wax is reached, the oil content will also be at the desired figure. This method of blending sweatings gives more satisfactory results than blending on the basis either of oil content or melting point.

In practice a number of schemes are possible, but the scheme adopted should be so arranged that adjustments can be made to suit the requirements for various grades, with the minimum change in composition of the products produced. A typical scheme of operating is given, whilst Table XII gives analyses of different fractions on which this scheme is based.

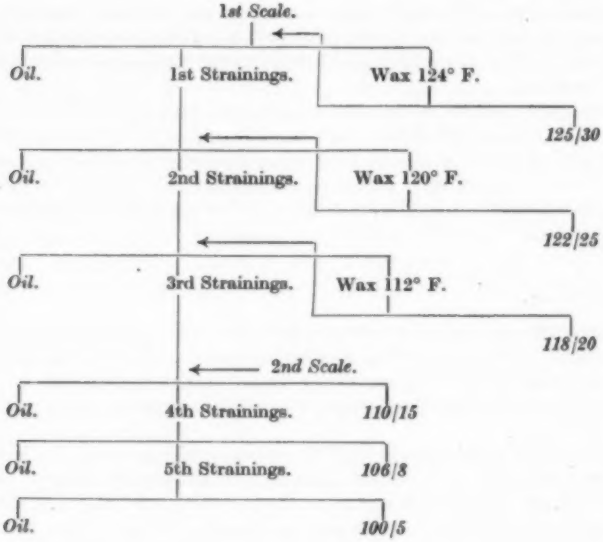


TABLE XII.

Analyses of Scales and Strainings.

	Melting Point, ° F.	Oil Content, %.	Melting Point of Oil-free Scale, ° F.
1st Scale	118	15	122
1st Strainings	108	20	113
2nd ,,	104	20	109
3rd ,,	98	15	102
2nd Scale	97	25	103
4th Strainings	96	15	100
5th ,,	93	20	98

The stoves are charged with scale at such a temperature that solidification does not take place immediately, and are allowed to cool. During the sweating the temperature is raised very slowly at the beginning and up to the point where fractions of melting point below 90° F. are collected. The temperature is then quickly raised to a fixed maximum, depending on the fraction being sweated, and is maintained at that figure until the sweating is finished. This slow sweating at the beginning gives better separation between oil and wax, and so reduces the amount of re-sweating to be done.

When the yield of wax from any particular sweating is low, double sweating is resorted to. By this means the quantity of wax per house is increased and at the same time a better product is obtained. The amount of sweating and re-sweating carried out can be judged from the fact that for every ton of finished wax produced, 4½ tons of scale or sweatings are dealt with.

To obtain uniform products throughout the range, it is important that the two scales charged to the sweating plant should be of constant composition and the different grades of waxes should then always be prepared in the same way.

(*d*) *Decolorizing.*

The waxes from the sweating plant are still too high in colour to be despatched without further treatment. The colour is removed and the different grades are prepared to colour specification by running the melted waxes through previously ignited Florida earth of 16–30 mesh per inch, contained in tall vertical columns. The wax to be treated is settled until free from moisture, and then filtered through the Florida earth at a definite rate, the temperature being kept as low as possible. The colour of the filtered wax is very low at the start of the run and gradually rises, the filtration being stopped when the bulk of filtered wax is of the necessary colour.

The filters are allowed to drain and the Florida earth is then washed free from wax by circulating naphtha through the filters. The naphtha is then removed by steaming, and the Florida earth reactivated by heating in an oil-burning rotary furnace at a temperature of 900° F. The mixture of naphtha and wax is separated by steam distillation, the naphtha being used again and the wax returned for re-sweating. The quantity of wax returned amounts to 20 per cent. of the wax decolorized.

The quantity of Florida earth used for decolorizing is about half a ton for every ton of decolorized wax obtained, whilst the fresh earth necessary as make up for mechanical loss amounts to 0·04 of a ton per ton of wax.

(*e*) *Finished Waxes.*

The molten wax is cast into trays of capacity 14 lb. and allowed to cool at atmospheric temperature, care being taken that the temperature before casting is not too low, otherwise rough-surfaced cakes are obtained due to the wax solidifying too quickly.

The waxes of melting point above 118° F. are comparatively transparent, whilst those of lower melting point are more or less opaque. All grades, however, are more transparent than corresponding grades prepared by rapid

cooling, as in press moulding. Opaqueness and mottling in waxes cast at atmospheric temperature have been found to be due to the presence of air and oil and the removal of either results in transparent wax, free from mottling.

All grades are run to a definite melting point and colour, but to meet the specification for certain grades, special tests have to be applied. These include loss on heating at a given temperature, penetration and plasticity tests. Over and above these tests, however, all waxes are examined daily in the Jackson–Burmah testing machine which determines oil content and width of cut.

IV. Refining to Maximum Spirit.

(*a*) *Straight-run Spirit.*

The oil products from the retorting of shale consist of scrubber naphtha and crude oil in the ratio of 15 to 85. Of the former 95 per cent. is within the motor-spirit range, and of the latter 5 per cent. giving a total yield of spirit existing as such in the scrubber naphtha and crude oil of 18·5 per cent. In refining, the crude oil is topped and the distillate to 200° C. is added to the scrubber naphtha and the blend refined as a whole. The refining of this material to specification presents no special difficulties. The crude spirit is treated with sulphuric acid (sp. gr. 1·84) and caustic soda in a pump orifice washer and re-run in a pipe-still unit, the distillate being finished by plumbite treatment.

As well as motor spirit, various grades of solvents are prepared from this same base stock. These solvents are used in the rubber, linoleum and cleaning industries, and are excellent solvents due to their comparatively high proportion of unsaturated compounds.

(*b*) *Cracking.*

The residue distilling above 200° C. can be converted into motor spirit either by cracking or hydrogenation. Both methods have been investigated experimentally, but the former has been general commercial practice during the past nine years.

Shale oil is comparatively easily cracked, and when working to maximum spirit production low-pressure liquid phase operation gives satisfactory results. At 795–800° F. and 175 lb. per sq. in. pressure, crude shale oil and shale-gas oil yield respectively approximately 55 and 65 per cent. spirit. As would be expected, however, the spirit under these cracking conditions is of low Octane No. Working at higher temperatures, 1000–1100° F., either under pressure or on vapour-phase operation, gas oil and kerosene give lower yields of higher Octane No. spirit. In one test, kerosene and pressure distillate bottoms from the liquid phase plant were cracked in a vapour-phase unit at 1100° F. and gave the following yields :—

Spirit	52% by volume.
Fuel oil	10% ,,
Gas, loss and coke . . .	38% ,,

In this case the Octane No. of the spirit was 70, but, as seen, the yield was very low compared with the low-pressure cracking of this stock, which

yielded 70–75 per cent. spirit. This yield of spirit could be raised to approximately 60 per cent. by increasing the pressure to 800–1000 lb. per sq. in.

While in the existing units only crude oil and gas oil have been processed individually, the relative yields and ease of cracking of various cuts from shale oil have been determined in the laboratory autoclave, and these yields by the use of known factors can be converted into commercial yields. In this series of tests all distillations were carried out cracking to coke at a pressure of 150 lb. per sq. in. All experiments were carried out under exactly the same conditions, and yields are strictly comparable.

Cracking Stock.	Yield of Cracked Spirit, % by volume.
Crude shale oil	62·0
Crude shale oil distillate	63·0
Acid and soda treated crude shale oil distillate	65·7
Blue oil	65·0
Heavy oil and paraffin	68·4
Paraffin wax	78·9
Kerosene	83·0

Refining of Cracked Spirit.

Cracked shale spirit as produced by liquid-phase low-pressure cracking is more saturated than spirit recovered from the retort gases, and this probably explains the comparatively low octane rating.

	Spirit Recovered from Shale Retort Gas, %.	Cracked Spirit from Shale Oil, %.
Saturated hydrocarbons	42·5	56·0
Unsaturated hydrocarbons	48·0	32·0
Naphthenes	9·5	12·0
Aromatic hydrocarbons	Nil.	Nil.

The principal impurities to be removed are pyridine bases, phenolic bodies and gum-forming unsaturated hydrocarbons. As with straight-run spirit, the most successful refining agent known at present is sulphuric acid, but in this case to remove the bulk of the phenols (which amount to 1 per cent.), a preliminary soda treatment is necessary. The refining scheme therefore consists of caustic soda, acid, caustic soda and re-running, followed by plumbite and sulphur treatment of the distillate. Several interesting features present themselves in this operation. The acid treatment must be controlled within fairly narrow limits; a low acid treatment leaves pyridine bases in the spirit, with consequent bad smell, which is not removed by the subsequent sweetening process. On the other hand, too much acid gives a distillate of high SO_2 content, which requires excess soda to neutralize it before plumbite, and at the same time the pressure distillate residue becomes acidic, and is therefore not at all suitable for cracking stock. Excess acid treatment also results in carbon formation in the pipe-still and tower, thereby reducing the time efficiency of the unit.

To prevent the formation of SO_2, re-running of pressure distillate should be carried out at as low a temperature as possible. High temperatures favour the evolution of SO_2, which must be removed, since it adversely affects the subsequent plumbite treatment and causes severe corrosion of the distillation equipment.

The plumbite process employed is of the type where plumbite is regenerated *in situ*, and is conducted on the batch system with pump circulation. The mercaptan content of the spirit is 0·005 per cent. and average plumbite and sulphur consumption works out at about 0·125 per cent. plumbite solution (0·2 lb. PbO and 1·5 lb. NaOH per gallon) and 0·0002 lb. per gallon of sulphur. The presence of phenols complicates the operation as, should the preliminary soda wash be inefficient, the concentration of caustic soda decreases rapidly and the lead combines with phenols. In particularly bad batches this is evident by the spirit going off colour and ultimately throwing down a deposit of lead phenates, but it is possible to get an apparently water-white clear spirit which, on exposure to light and/or heat, becomes cloudy. It has been shown that by washing the spirit with water, the lead phenates, even from apparently clear and colourless spirit, are removed as a sludge, so that water-washing becomes a necessary operation to ensure a satisfactory product. Another feature of the plumbite when applied to shale cracked spirit is that the small quantity of phenols still in the spirit is extracted by the caustic soda, and the sodium phenate solution so formed at the same time is oxidized, and ultimately this coloured material redissolves in the spirit, and is not removed by washing with water. At this stage the plumbite solution must be discharged, and so a careful control of the preliminary soda wash is essential.

(*c*) *Hydrogenation.*

Theoretically hydrogenation is the most efficient way of refining shale oil, and actually yields of 100 per cent. by volume and over can be realized. In all other known methods of refining, these troublesome compounds, pyridine bases and phenols, peculiar to shale and coal oils, have to be removed, and incidentally the most active unsaturated hydrocarbons are lost. In hydrogenation, however, the elements, nitrogen, oxygen and sulphur, are replaced by hydrogen, and the unstable olefines and diolefines become saturated to the more stable paraffins.

Scotch shale oil can readily be hydrogenated to motor spirit. Various methods of treating the material are possible, and one method by which yields of slightly over 100 per cent. by volume can be realized is briefly outlined.

The shale oil is first distilled, leaving a residue above the diesel oil range. This residue is hydrogenated in the liquid phase whereby it is converted into 5 to 10 per cent. motor spirit and gas oil plus recycle oil. These are separated by distillation, the gas oil blended with the distillate from the topping unit and the blend subjected to hydrogen in the vapour phase. The products of this operation are spirit and re-cycle oil, which are again separated by distillation and the gas oil re-cycled. The benzine produced is water-white, and only requires a caustic-soda wash to make it marketable. The Octane No. of motor spirit so produced is low—about 51–54.

The Octane No., however, can be increased, but unfortunately only at the expense of yield. Two methods of raising the Octane No. are—hydrogenation at a higher temperature or re-forming. It has been estimated that to get an Octane No. of 72 by the former method, the yield would be reduced by 17–20 per cent. by volume. By reforming, the Octane rating could probably be increased by about 10 Octane Nos. with a decrease in yield of 20 per cent.

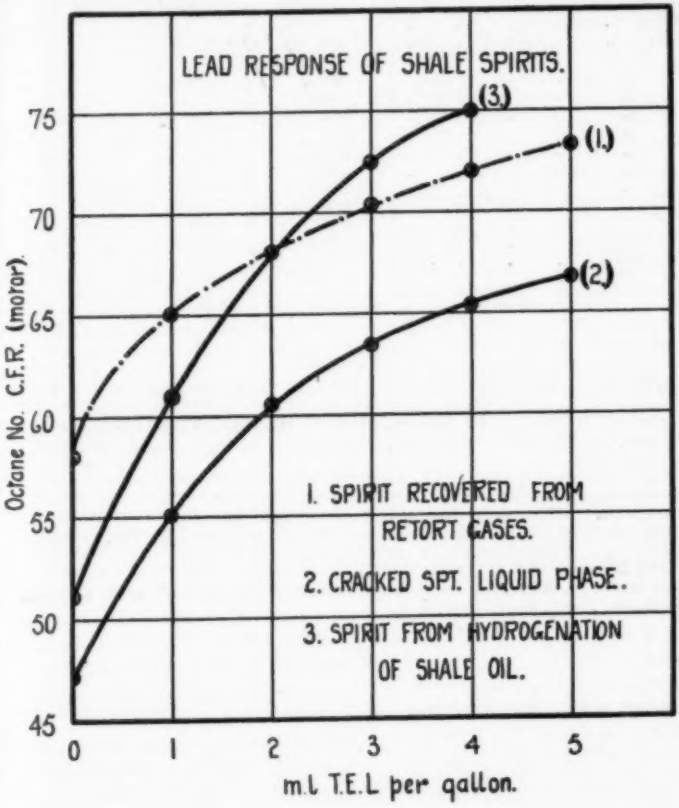


FIG. 4.

Another method of increasing the octane rating is by the addition of tetra-ethyl lead, and in this case, probably owing to the comparative freedom of the spirit from sulphur, the lead response is very good; the addition of 2·5 mls. per gallon is sufficient to raise the Octane No. from 54 to 70.

For comparison, analyses of shale straight-run spirit, shale cracked spirit, and the spirit obtained by hydrogenation of shale oil are given in Table XIII. The lead response curves of these three spirits are shown in Fig. 4.

TABLE XIII.

	Spirit Recovered from Retort Gases.	Cracked Spirit Liquid Phase.	Spirit from Hydrogenation of Shale Oil.
Sp. gr.	0·732	0·740	0·720
Iodine value (Wijs 1 hr.)	116	85	—
Bromine No.	60	40	—
Aniline point	42·0° C.	48·3° C.	60·3° C.
Sulphur	0·06%	0·10%	0·003%
I.B.P.	49° C.	36° C.	38° C.
10% dist. at	79 ,,	71 ,,	70 ,,
20% ,,	88 ,,	92½ ,,	87 ,,
30% ,,	96 ,,	111 ,,	100 ,,
40% ,,	104 ,,	126 ,,	112 ,,
50% ,,	111 ,,	139½ ,,	122 ,,
60% ,,	119 ,,	151½ ,,	134 ,,
70% ,,	127½ ,,	163 ,,	145 ,,
80% ,,	138 ,,	174 ,,	158 ,,
90% ,,	152 ,,	185 ,,	174 ,,
F.B.P.	178 ,,	200 ,,	194 ,,
Total distillate	98·0%	98·0%	98·0%
Residue	1·0%	1·0%	1·0%
Loss	1·0%	1·0%	1·0%

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THE VISCOSITIES OF HYDROCARBONS.

By E. B. Evans, Ph.D., M.Sc. (Member).

PARTS VII AND VIII.*

Synopsis.

The two following sections of this paper collect and correlate the data on the viscosities of monocyclic aromatic and polycyclic hydrocarbons respectively, and complete the survey of data.

Part VII contains data on nineteen monocyclic aromatic hydrocarbons with from six to sixty carbon atoms and covering a very wide range of viscosity. Data on ten of these are from the work of Mikeska, whilst the author has examined *n*-propylbenzene and *n*-butylbenzene, on which there were previously very little data.

The hydrocarbons dealt with in Part VIII under the heading "polycyclic" are sixty-two in number, and comprise all those hydrocarbons containing two or more ring structures. They contain from nine to thirty-eight carbon atoms, and many of them may be of interest in connection with the composition and properties of lubricating-oil fractions.

Data on the hydrocarbons summarized in Tables XLV and XLVI are due to Mikeska (thirty-six compounds), Landa and Čech (six), Leder (five) and the author, who has examined fifteen hydrocarbons.

Many of the hydrocarbons considered have high melting points, and for this and other reasons the range of temperatures over which measurements were made is sometimes restricted. The data have then had to be extrapolated considerably in order to obtain the final tables. It is believed that the results are accurate within the limitations of the original data. As the experimental figures are also tabulated elsewhere in the paper, checks may readily be made in individual cases.

PART VII.

The Viscosities of the Monocyclic Aromatic Hydrocarbons.

There is somewhat more information available on the viscosities of the aromatic hydrocarbons, but only eleven compounds have been examined, and on some of these only one measurement has been made. A number of investigators have considered benzene, and the International Critical Tables give values from 0° to 70°, which are a composite of the best values up to 1926. Thorpe and Rodger record data on toluene, ethylbenzene and the three isomeric xylenes, over a considerable temperature range. Timmermans and Martin's results are only at the temperatures of 15° and 30°, with the addition of 60° in the cases of benzene and toluene. Heydweiler [46] gives values for toluene at three temperatures from about 20°

* Paper received September 22nd, 1938.

to 100°, and there are isolated values for benzene and toluene by Lewis [47] and by Kendall and Monroe.[48] The data for benzene and toluene are generally in excellent agreement with the exception of Lewis' value for benzene at 25°, which is about 2 per cent. lower than the mean value.

The data on ethylbenzene, while less extensive, are not in such good accord. Thorpe and Rodger's results fall well on the mean curve through all the data, and are somewhat higher—about 2 per cent.—than the two results of Timmermans and Martin. The isolated measurement of Dunstan, Hilditch and Thole at 25° also supports Thorpe's figures, which have the added advantage of covering the range from 0° to 131° and plotting very regularly.[49]

Timmermans and Martin's two results on each of *m*- and *p*-xylene (they did not measure *o*-xylene) leave nothing to be desired in their agreement with Thorpe and Rodger's results. Hilditch and Dunstan [50] are responsible for the sole measurements on phenylacetylene and on styrene, at 25°, whilst Dunstan, Hilditch and Thole have made measurements on *n*-propylbenzene and Thole on *n*-butylbenzene and *o*-cymene at the same temperature.

The author's own measurements are confined to *n*-propylbenzene and *n*-butylbenzene over the range from 5° to 90° C. For *n*-propylbenzene our results are ½–1 per cent. higher than Timmermans' values at 15° and 30°, and the figure of Dunstan, Hilditch and Thole is also a little lower than the author's. For *n*-butylbenzene the discrepancies are rather greater. Timmermans' value at 15° is 3–4 per cent. lower than ours, but at 30° only about 1 per cent. lower. As we have seven determinations which plot regularly against the two values of Timmermans and Martin, and bearing in mind the fact that the difference is not constant, as would be approximately the case if impurity of the compounds used were the main cause of the discrepancy, the presumptions are in favour of our values. Thole's figure at 25° is over 7 per cent. higher than our own, and even more in excess of the figure of Timmermans.

More recently a number of aromatic hydrocarbons with long paraffinic or olefinic side-chains have been prepared and examined—*e.g.*, cetylbenzene [51] and ten hydrocarbons recorded by Mikeska,[52] and containing 24–60 carbon atoms. Mikeska's measurements (in centistokes) generally cover the range 37·8–98·9° C., but as many of these long-chain aromatic derivations melt at fairly high temperature, a viscosity measurement at 37·8° C. was not always obtainable. In these cases, to obtain the data given in the summarized Tables XXXIX and XL, considerable extrapolation has been necessary for the lower temperatures. The Ubbelohde chart has been used for this purpose, the absolute viscosities being obtained by conversion from the kinematic values read off from the curve.

The Preparation of Aromatic Hydrocarbons.

n-Propylbenzene was prepared by the action of diethyl sulphate on benzyl magnesium chloride according to the method of Gilman and Meyers.[53] The maximum yield obtained after purification by long refluxing over sodium wire and subsequent fractionation was 53 per cent., the product

boiling at 158·6° C. ± 0·7° C. Repeated fractionation did not narrow this range appreciably.

The Wurtz reaction was employed in the synthesis of *n*-butylbenzene. Radziswewski [54] stated that an almost theoretical yield of this hydrocarbon is obtained by heating benzyl chloride and propyl bromide, together with sodium, for several hours on the sand-bath. It is highly improbable that this should be the case, as it is difficult to conceive why, when each of the halides will condense independently with sodium, a mixture should react exclusively in the desired manner. Actually, experiment showed that much dibenzyl and *n*-hexane were formed, the yield of impure butylbenzene being only 17–18 per cent. The method used by Stratford,[55] who claimed a 30–32 per cent. yield by condensing bromobenzene with butylbromide, is far more satisfactory. Similar yields were obtained, using this method. The hydrocarbon was purified by long refluxing over sodium and re-fractionation.

The physical constants of these aromatic hydrocarbons are given in Table XXXIV.

TABLE XXXIV.

The Properties of the Aromatic Hydrocarbons.

Hydrocarbon.	*n*-Propylbenzene.	*n*-Butylbenzene.
Boiling point (corr.) . .	158·6 ± 0·7	182·1–183·1
d_4^{15}	0·8666	0·8708
d_4^{20}	0·8628	0·8668
n_D^{20}	1·4919	1·4880
Aniline point	Below −30° C.	Below −30° C.

TABLE XXXV.

I.C.T. Composite Data.		Heydweiller.		Thorpe and Rodger.									
Benzene.		Toluene.		Toluene.		Ethylbenzene.		*o*-Xylene.		*m*-Xylene.		*p*-Xylene.	
T, ° C.	η.	T, ° C.	η.	T, ° C.	η.	T, ° C.	η.	T, ° C.	η.	T, ° C.	η.	T, ° C.	η.
0	0·900	20·6	0·583	0·26	0·7655	0·41	0·869	0·49	1·095	0·24	0·799	8·28	0·752
10	0·757	78·2	0·323	9·88	0·6683	11·41	0·744	13·88	0·881	11·52	0·684	20·53	0·639
20	0·647	100	0·272	19·47	0·5900	21·66	0·654	26·54	0·738	23·36	0·595	31·23	0·561
30	0·561			30·25	0·5184	32·90	0·572	39·33	0·628	35·97	0·513	41·85	0·498
40	0·492			39·86	0·4667	47·11	0·491	51·94	0·544	48·71	0·450	53·59	0·441
50	0·436			49·43	0·4219	60·51	0·430	65·41	0·473	59·94	0·404	64·87	0·396
60	0·389			60·18	0·3799	73·81	0·381	78·78	0·416	60·27	0·403	77·27	0·353
70	0·350			69·13	0·3503	83·62	0·349	90·82	0·373	71·20	0·366	88·87	0·320
				80·59	0·3164	95·60	0·316	101·78	0·340	86·35	0·322	100·84	0·290
				91·74	0·2877	107·97	0·287	116·61	0·302	98·68	0·293	111·83	0·267
				99·95	0·2695	119·19	0·263	128·15	0·276	109·75	0·269	123·26	0·245
				107·08	0·2554	131·40	0·241	141·14	0·252	123·53	0·244	135·21	0·225
										135·28	0·225		

TABLE XXXVI.

Hydrocarbon.	η at 15° C.	η at 25° C.	η at 30° C.	Authors.
Benzene	0·696	—	0·566 [1]	Timmermans and Martin.
,,	—	0·5961	—	Lewis.
Toluene	—	0·5520	—	Kendall and Monroe.
,,	—	0·5512	—	Lewis.
,,	0·623	—	0·523 [2]	Timmermans and Martin.
Ethylbenzene	—	0·632	—	Dunstan, Hilditch and Thole.
,,	0·697	—	0·581	Timmermans and Martin.
m-Xylene	0·650	—	0·547	,, ,,
p-Xylene	0·682	—	0·568	,, ,,
n-Propylbenzene	—	0·793	—	Dunstan, Hilditch and Thole.
,,	0·917	—	0·746	Timmermans and Martin.
n-Butylbenzene	—	1·05	—	Thole.
,,	1·090	—	0·895	Timmermans and Martin.
o-Cymene	—	1·02	—	Thole.
Phenylacetylene	—	0·886	—	Hilditch and Dunstan.
Styrene	—	1·11	—	,, ,,
Temp.	29·8°	49·8°	70·0°	
Cetylbenzene	8·05	4·77	3·15	Fuel Research Board.

[1] 0·395 at 60° C. [2] 0·587 at 60° C.

TABLE XXXVII.

Author's Data.

Hydrocarbon.	η at 5° C.	η at 15° C.	η at 30° C.	η at 45° C.	η at 60° C.	η at 75° C.	η at 90° C.
n-Propylbenzene	1·083	0·9181	0·7452	0·6186	0·5266	0·4527	0·3934
n-Butylbenzene	1·351	1·139	0·9035	0·7406	0·6237	0·5283	0·4586

TABLE XXXVIII.

Data of Mikeska—Viscosities in Centistokes.

No.	Hydrocarbon.	T, ° C.	ν.	T, ° C.	ν.	T, ° C.	ν.	T, ° C.	ν.	T, ° C.	ν.
1	Octadecylbenzene	37·8	9·28	56·6	5·87	64·0	5·05	77·2	3·90	98·9	2·78
2	Docosylbenzene	—	—	54·4	9·2	64·4	7·55	—	—	98·9	3·48
3	(1-Butyloctadecyl) benzene	37·8	16·57	56·7	9·24	64·5	7·46	—	—	98·9	3·72
4	(1-Butyldocosyl) benzene	37·8	23·90	—	—	64·4	10·8	—	—	98·9	5·0
5	(1-Butyloctadecen-1-yl)benzene	37·8	14·57	56·6	8·64	64·4	6·91	77·5	5·28	98·9	3·51
6	(1-Butyldocosen-1-yl)-benzene	37·8	22·10	—	—	64·4	10·2	—	—	98·9	5·95
7	Dioctadecylbenzene	37·8	47·9	—	—	—	—	78·7	15·70	98·9	9·46
8	Trioctadecylbenzene	37·8	97·7	54·4	49·6	64·4	35·81	74·1	26·26	98·9	14·56
9	(1-Butyloctadecyl) (1-butyloctadecen-1-yl)-benzene	—	—	54·4	42·68	65·6	30·03	77·2	21·07	98·9	12·47
10	Di(1-butyloctadecyl)-benzene	—	—	—	—	65·2	28·57	78·3	19·34	98·9	11·74

Note.—Numbers in first column refer to those given in Mikeska's paper.[1]

TABLE XXXIX.

TABLE XXXIX.

Viscosities of the Monocyclic Aromatics.

Hydrocarbon.	Empirical Formula.	Mol. Wt.	Viscosity in cp. at					Source of Data.	Remarks.
			0° C.	20° C.	50° C.	80° C.	100° C.		
Benzene	C_6H_6	78	0·9015	0·6515	0·4365	0·317	0·2655	Composite	
Toluene	C_7H_8	92	0·764	0·5835	0·417	0·3135	0·2665	,,	
Ethylbenzene	C_8H_{10}	106	0·877	0·668	0·4785	0·3595	0·305	Thorpe and Rodger	
o-Xylene	C_8H_{10}	106	1·102	0·813	0·556	0·411	0·3445	,, ,,	
m-Xylene	C_8H_{10}	106	0·8015	0·6165	0·4445	0·3375	0·2885	,, ,,	
p-Xylene	C_8H_{10}	106	0·8455	0·6425	0·458	0·3435	0·291	,, ,,	
n-Propylbenzene	C_9H_{12}	120	1·178	0·859	0·589	0·4315	0·362	Author	
n-Butylbenzene	$C_{10}H_{14}$	134	1·478	1·050	0·7015	0·5045	0·420	,,	
Cetylbenzene	$C_{22}H_{38}$	300	—	10·90	4·75	2·68	—	Fuel Research Board	M. pt. 27° C.
Octadecylbenzene (1)	$C_{24}H_{42}$	330	29·0	13·25	5·70	3·08	2·22	Mikeska	M. pt. 35–36° C.
(1-Butyloctadecen-1-yl)benzene (5)	$C_{28}H_{48}$	384	68·45	25·5	8·77	4·17	2·82	,,	
Docosylbenzene (2)	$C_{28}H_{50}$	386	70·70	25·5	8·60	4·05	2·93	,,	M. pt. 42–44° C.
(1-Butyloctadecyl)benzene (3)	$C_{28}H_{50}$	386	78·35	28·15	9·40	4·39	2·95	,,	M. pt. 38° C.
(1-Butyldocosen-1-yl)benzene (6)	$C_{32}H_{56}$	440	43·55	23·25	11·21	6·44	4·77	,,	
(1-Butyldocosyl)benzene (4)	$C_{32}H_{58}$	442	138·2	45·40	13·90	6·05	3·95	,,	M. pt. 32–33° C.
Dioctadecylbenzene (7)	$C_{42}H_{78}$	582	186·4	71·85	24·70	11·31	7·51	,,	M. pt. 69–70° C.
(1-Butyloctadecyl) (1-butyloctadecen-1-yl)benzene (9)	$C_{46}H_{86}$	692	536·9	156·4	41·90	16·26	9·92	,,	M. pt. 31·5° C.
Di-(1-butyloctadecyl)benzene (10)	$C_{46}H_{90}$	694	546·5	153·0	39·95	15·15	9·22	,,	M. pt. 64–66° C.
Trioctadecylbenzene (8)	$C_{60}H_{114}$	834	581·3	178·8	48·60	19·04	11·53	,,	M. pt. 46·5–47·0° C.

Note.—Numbers following names of hydrocarbons refer to those in Mikeska's paper.

TABLE XL.

Kinematic Viscosities—Aromatics.

Hydrocarbon.	d^0.	d^{50}.	d^{100}.	0° C.	20° C.	50° C.	80° C.	100° C.
Benzene	0·8952	0·8532	0·8112	1·007	0·7415	0·5115	0·383	0·3275
Toluene	0·8816	0·8406	0·7996	0·8665	0·6745	0·4960	0·3840	0·3334
Ethylbenzene	0·8854	0·8414	0·7974	0·9905	0·7970	0·5685	0·4410	0·3825
o-Xylene	0·8972	0·8572	0·8172	1·228	0·9225	0·6485	0·4935	0·4215
m-Xylene	0·8811	0·8384	0·7957	0·9095	0·7140	0·5305	0·4150	0·3625
p-Xylene	0·8783	0·8350	0·7917	0·9630	0·7460	0·5485	0·4245	0·3675
n-Propylbenzene	0·8786	0·8390	0·7995	1·341	0·9955	0·7020	0·5290	0·4530
n-Butylbenzene	0·8824	0·8434	0·8044	1·674	1·212	0·8320	0·6150	0·5220
Cetylbenzene	0·8730	0·8397	0·8064	—	12·68	5·656	3·269	—
Octadecylbenzene (1)	0·8696	0·8384	0·8052	33·0	15·45	6·8	3·76	2·76
(1-Butyloctadecen-1-yl)-benzene (5)	0·8830	0·8520	0·8210	77·5	29·3	10·3	5·0	3·43
Docosylbenzene (2)	0·8674	0·8351	0·8028	81·5	29·8	10·3	4·96	3·40
(1-Butyloctadecyl)-benzene (3)	0·8706	0·8394	0·8081	90·0	32·8	11·2	5·35	3·65
(1-Butyldocosen-1-yl)-benzene (6)	0·8729	0·8434	0·8142	49·9	27·0	13·3	7·8	5·86
(1-Butyldocosyl)benzene (4)	0·8692	0·8372	0·8058	159·0	53·0	16·6	7·4	4·9
Dioctadecylbenzene (7)	0·8669	0·8371	0·8072	215·0	84·0	29·5	13·8	9·3
(1-Butyloctadecyl)(1-butyloctadecen-1-yl)-benzene (9)	0·8660	0·8380	0·8100	620·0	183·0	50·0	19·8	12·25
Di(1-butyloctadecyl)-benzene (10)	0·8620	0·8320	0·8020	634·0	180·0	48·0	18·6	11·5
Trioctadecylbenzene (8)	0·8676	0·8338	0·8090	670·0	209·0	58·0	23·2	14·25

Note.—Numbers following names of hydrocarbons refer to those in Mikeska's paper.

PART VIII.

The Viscosities of the Polycyclic Hydrocarbons.

In the group of polycyclic hydrocarbons are included all hydrocarbons with two or more ring structures in the molecule, either saturated or unsaturated. These compounds are of great interest and importance, since they probably form the major part of petroleum lubricating oils. The difficulties of synthesis and purification have resulted in very little information being available until recently on the viscosities or other physical properties of these hydrocarbons.

The commonest bicyclic hydrocarbons are represented by naphthalene and its derivatives: naphthalene has been examined by Kurnakov and others,[56] and tetrahydronaphthalene and decahydronaphthalene by Herz and Schuftan.[57] Thole [58] has also measured the viscosity of tetrahydronaphthalene at 25° C. Kurnakov has determined viscosities of diphenylmethane at 100° C. and triphenylmethane at 95° and 100° C.

In several of these cases there is not enough data to plot: in others, notably in that of Kurnakov's data for naphthalene, the figures plot so irregularly as to be valueless. Moreover, in the only cases where a comparison is possible, that of tetrahydronaphthalene, Herz and Schuftan give 2·00 cp. at 25° C., while Thole gives 2·14.

Bingham and Fornwalt [17] determined the fluidities of diphenyl at several temperatures, and from these the corresponding viscosities have been calculated. This seems to be careful and reasonably complete data.

Lerer [24] has prepared and examined a number of very complex naphthalene and anthracene derivatives, which are of great interest. Judged by the results obtained by plotting, these data are reasonably

accurate and comprehensive, and deal with compounds far more viscous than have hitherto been examined.

Our own work on these hydrocarbons is confined to the simpler compounds with up to fourteen carbon atoms in the molecule. The measurements cover at least 50° C. range of temperature (in most cases 85°), with a minimum of five temperatures, the results plotting smoothly in all cases.

The compounds investigated include naphthalene and its tetra- and deca-hydro-derivatives, and the two methyl-naphthalenes, diphenyl, dibenzyl, di*cyclo*pentyl, di*cyclo*hexyl, phenyl*cyclo*hexane, phenyl*cyclo*pentane, and di*cyclo*hexylethane. The only comparison which can usefully be made is of the results on diphenyl, our results agreeing within 1 per cent. with those of Bingham and Fornwalt.

Our knowledge of the viscosities of polycyclic hydrocarbons has been extended enormously by the recent work of Landa and Čech,[59] and particularly of Mikeska.[52] Landa and Čech have investigated six hydrocarbons with twenty-eight or thirty carbon atoms—namely, the diphenyl derivatives of hexadecene, the phenylbenzyl derivatives of heptadecene and the various hydrogenation products of these. These data cover the temperature range 20–99° C. (in one case 0–99° C.) and plot well, with the exception of that on 1-phenyl-2-benzyl-heptadecene-2, which does not give a straight line on A.S.T.M. chart "C."

Mikeska's work covers thirty-seven hydrocarbons of the "polycyclic" class, these being naphthalene or diphenyl derivatives with paraffinic or olefinic side-chains and having total numbers of carbon atoms ranging from

TABLE XLI.

Kurnakov, Krotkov and Oksman.		Herz and Schuftan.		Thole.		Herz and Schuftan.		Kurnakov, etc.				Dover and Hensley.	
Naphthalene.		Tetrahydro-naphthalene.		Tetrahydro-naphthalene.		Decahydro-naphthalene.		Diphenyl-methane.		Triphenyl-methane.		Di-*m*-tolyl-ethane.	
T.	η.	T.	η.	T.	η.	T.	η.	T.	η.	T.	η.	T.	η.
80	0·886	25	2·00	25	2·14	25	2·41	100	0·83	95	3·5	5	11·915
90	0·759	50	1·30			50	1·58			100	3·22	12	9·569
150	0·217	75	0·906			75	1·08					22	6·349
156	0·196											32	4·688
												42	3·484

Lerer.										Bingham and Fornwalt.	
Dihydro-diethyl-anthracene.		Di*iso*butyl naphthalene.		1 : 2 : 3 : 4-Tetrahydro-1 : 4-di*iso*butyl-naphthalene.		Dihydrodi-*iso*amyl-anthracene.		Dihydrodi-*β*-octyl-anthracene.		Diphenyl.	
T.	η.	T.	η.	T.	η.	T.	η.	T.	η.	T.	η.
20·0	157	20·0	47·6	20·0	40·3	20·0	5086	15·0	2660	70·0	1·488
35·0	42·2	34·4	18·1	34·5	17·1	34·5	790	25·9	806	80·0	1·246
49·5	17·4	54·8	7·0	55·0	7·2	56·5	108	35·0	351	90·0	1·078
70·0	7·3	70·7	4·3	71·0	4·3	76·0	30	50·0	116	100·0	0·971
								59·0	66		

TABLE XLII.

Results of Landa and Čech.

Temp., ° C.	1 : 1-Diphenylhexadecene-1.	1 : 1-Diphenylhexadecane.	1 : 1-Di-*cyclo*hexylhexadecane.	1-Phenyl-2-benzylheptadecene-2.	1-Phenyl-2-benzylheptadecane.	1-*cyclo*-Hexyl-2-hexahydrobenzylheptadecane.
0	—	—	—	—	—	242·294
10	—	—	—	—	—	118·931
20	46·753	47·127	70·764	78·754	81·474	62·949
30	29·522	28·852	41·302	42·887	48·502	37·899
40	19·113	18·954	25·862	25·729	28·130	24·298
50	13·120	12·978	17·326	16·565	18·387	16·119
60	9·434	9·365	12·278	11·899	12·673	11·573
70	7·131	7·114	8·948	8·789	9·236	8·463
80	5·550	5·533	6·856	6·697	7·019	6·491
90	4·390	4·476	5·430	5·322	5·456	5·116
99	3·763	3·750	4·403	4·360	4·455	4·313

TABLE XLIII.

Viscosities of Polycyclic Compounds in cp.

(Own results.)

Hydrocarbon.	5° C.	15° C.	30° C.	45° C.	60° C.	75° C.	90° C.	105° C.	120° C.	135° C.	150° C.
Naphthalene	—	—	—	—	—	85° C.) 0·8974)	0·8465	0·7160	0·6243	0·5374	0·4755
1-Methylnaphthalene	5·140	3·849	2·598	1·909	1·469	1·179	0·9632				
2-Methylnaphthalene	—	—	40° C.) 1·685)	1·540	1·203	0·9707	0·8052				
1 : 2 : 3 : 4-Tetrahydronaphthalene	3·145	2·485	1·829	1·406	1·121	0·9206	0·7716				
Decahydronaphthalene	3·676	2·918	2·161	1·665	1·304	1·057	0·8768				
Dibenzyl	—	—	—	55° C.) 2·083)	1·900	1·498	1·203	1·002			
Diphenyl	—	—	—	—	—	1·349	1·084	0·9003	0·7588	0·6485	
Di*cyclo*pentyl	1·776	1·512	1·213	1·006	0·8381	0·7168	0·6152				
Di*cyclo*hexyl	6·247	4·625	3·145	2·293	1·741	1·376	1·116				
Phenyl*cyclo*hexane	4·012	3·074	2·192	1·656	1·302	1·056	0·8766				
Phenyl*cyclo*pentane	2·391	1·956	1·510	1·204	0·9856	0·8281	0·7094				
*cyclo*Hexyl*cyclo*pentane	3·278	2·635	1·976	1·537	1·231	1·015	0·8476				
Di*cyclo*hexylethane	14·42	9·618	5·898	3·885	2·760	2·101	1·624				

sixteen to thirty-eight and molecular weights from 212 to 520. The temperature range covered is in most cases 100° F. (37·8° C.) to 210° F. (98·9° C.), but in some instances the melting point of the hydrocarbon is above 38° C., and the measurements are consequently over a more restricted range. Considerable extrapolation has therefore been necessary to complete the data for the summarized tables.

Thanks are due to Dr. Mikeska, who has kindly supplied us with fuller density data and also his nomenclature for these hydrocarbons, before publication of the full details. The data in general plot very well, using, for example, A.S.T.M. Chart "C," although in a few cases the plots are not so good. As regards the density data, no results are given for compound 52, and consequently the results for this hydrocarbon can only be given in centistokes. For twelve other compounds densities are recorded only at

TABLE XLIV.

Data of Mikeska.

(Viscosities in centistokes.)

No.	Hydrocarbon.	T. °C.	ν.	T. °C.	ν.	T. °C.	ν.	T. °C.	ν.	T. °C.	ν.
15	Octadecylnaphthalene	—	—	56·6	12·28	64·1	9·92	78·9	6·91	99·4	4·63
16	Docosylnaphthalene	—	—	—	—	64·4	14·8	98·9	6·53	135	3·54
17	(1-Butyloctadecyl)-naphthalene	37·8	35·31	54·4	18·88	65·4	13·42	—	—	98·9	5·84
18	(1-Butyloctadecen-1-yl)naphthalene	37·8	31·58	56·3	16·01	64·5	12·10	77·2	8·55	99·7	5·22
19	(1-Butyldocosyl)-naphthalene	—	—	54·4	21·60	64·4	15·76	—	—	98·9	6·74
20	(1-Butyldocosen-1-yl)-naphthalene	37·8	37·77	54·4	20·39	—	—	—	—	98·9	6·52
21	(2-Butyleicosyl)-naphthalene	—	—	—	—	64·4	15·98	73·3	12·63	98·9	6·75
22	(1-Ethyl-2-butyleicosen-1-yl)naphthalene	37·8	58·03	—	—	—	—	—	—	98·9	7·77
23	(1 : 2-Dibutyleicosyl)-naphthalene	37·8	68·76	54·4	33·34	—	—	—	—	98·9	8·57
24	(1 : 2-Dibutyleicosen-1-yl)naphthalene	—	—	—	—	64·2	21·64	79·7	13·44	98·9	8·25
25	(1-Ethyl-2-butyleicosyl)naphthalene	37·8	64·40	54·4	31·29	—	—	—	—	98·9	8·10
26	Hexylnaphthalene	37·8	4·82	54·4	3·14	64·2	2·48	78·1	1·97	98·9	1·41
27	Dihexylnaphthalene	37·8	19·11	54·4	10·51	64·4	7·67	77·8	5·36	98·9	3·40
28	Trihexylnaphthalene	37·8	32·67	54·4	17·20	—	—	—	—	98·9	5·09
29	Trihexylnaphthalene	37·8	41·77	54·2	21·39	65·7	14·79	—	—	98·9	6·00
30	Trihexylnaphthalene	—	—	—	—	—	—	—	—	—	—
31	Octadecyltetrahydronaphthalene	—	—	54·4	13·74	65·6	10·01	77·2	7·55	98·9	4·90
32	Docosyltetrahydronaphthalene	—	—	54·4	20·71	64·0	15·57	—	—	98·9	6·90
33	(1-Butyloctadecyl-tetrahydronaphthalene	37·8	51·87	54·4	26·12	67·0	16·61	—	—	98·9	7·10
34	(1-Butyloctadecen-1-yl)tetrahydronaphthalene	37·8	47·00	54·4	24·30	65·6	16·79	—	—	98·9	7·04
35	(1-Butyldocosen-1-yl)-tetrahydronaphthalene	37·8	60·95	54·4	29·81	64·4	22·46	—	—	98·9	8·52
36	(1-Butyldocosyl)tetrahydronaphthalene	37·8	68·39	54·4	33·42	64·0	23·75	—	—	98·9	9·11
37	Octadecyldecahydronaphthalene	—	—	54·4	16·79	65·7	12·38	—	—	98·9	5·86
38	Docosyldecahydronaphthalene	37·8	44·26	—	—	64·0	17·90	78·8	12·06	98·9	7·80
39	1-Butyloctadecyldecahydronaphthalene	37·8	52·93	54·4	26·87	—	—	—	—	98·9	7·61
40	Octadecyldiphenyl	—	—	—	—	80·2	8·08	98·9	5·49	109·4	4·47
41	(1-Butyloctadecen-1-yl)diphenyl	37·8	54·42	54·4	26·71	65·0	18·43	76·7	13·24	98·9	7·46
42	(1-Butyloctadecyl)-diphenyl	—	—	54·4	28·16	66·8	18·20	—	—	98·9	7·60
43	Docosyldiphenyl	—	—	—	—	98·9	7·07	108·6	5·80	115·6	5·21
44	(1-Butyldocosen-1-yl)-diphenyl	—	—	54·4	32·63	78·8	12·06	—	—	98·9	9·12
45	(1-Butyldocosyl-dl)-phenyl	—	—	54·4	36·12	—	—	79·9	15·79	98·9	9·71
46	(1-Butyloctadecyl-dl)-phenyl	37·8	77·12	54·4	36·22	67·2	22·43	—	—	98·9	9·10
47	1 : 1-Diphenyloctadecene-1	37·8	28·08	56·3	14·06	64·4	10·88	77·8	7·55	98·9	4·84
48	1 : 1-Diphenyloctadecane	37·8	26·35	56·3	13·56	64·1	10·70	77·8	7·37	98·9	4·68
49	1-Phenyl-1-naphthyloctadecene-1	37·8	88·36	54·4	39·26	65·4	24·84	76·7	16·65	98·9	8·91
50	5 : 14-Diphenyloctadecadiene-5 : 13	37·8	27·93	54·4	15·63	65·6	10·06	—	—	98·9	4·59
51	5 : 14-Diphenyloctadecane	37·8	33·35	54·4	20·07	65·6	11·58	—	—	98·9	4·99
52	5 : 14-Dicyclohexyloctadecane	37·8	51·28	54·4	28·03	65·6	16·11	—	—	98·9	6·37

TABLE XLV.

Hydrocarbon.	Empirical Formula.	Mol. Wt.	Viscosity in cp. at					Source of Data.	Remarks.
			0° C.	20° C.	50° C.	80° C.	100° C.		
Indene	C_9H_8	116	2·938	1·816	1·052	0·7345	0·5945	Author	
Hydrindene	C_9H_{10}	118	2·239	1·493	0·9185	0·6635	0·542	,,	
Naphthalene	$C_{10}H_8$	128	—	(2·483)	(1·422)	0·964	0·761	,,	0·6225 cp./120° C.; 0·5395 cp./150° C. M. pt. 80·5° C.
1 : 2 : 3 : 4-Tetrahydronaphthalene	$C_{10}H_{12}$	132	3·606	2·234	1·256	0·867	0·698	,,	
Decahydronaphthalene	$C_{10}H_{18}$	138	4·169	2·630	1·466	0·991	0·7815	,,	
Di*cyclo*pentyl	$C_{10}H_{18}$	138	1·923	1·403	0·9185	0·6775	0·560	,,	
α-Methylnaphthalene	$C_{11}H_{10}$	142	6·109	3·334	1·679	1·102	0·867	,,	
β-Methylnaphthalene	$C_{11}H_{10}$	142	—	(2·564)	1·361	0·910	0·721	,,	M. pt. 34·5C.
Phenyl*cyclo*pentane	$C_{11}H_{14}$	146	2·667	1·778	1·086	0·785	0·647	,,	
*cyclo*Hexyl*cyclo*pentane	$C_{11}H_{20}$	152	4·645	2·723	1·469	0·991	0·780	,,	
Diphenyl	$C_{12}H_{10}$	154	—	(3·733)	(1·959)	1·253	0·9595	,,	0·7585 cp./120° C. M. pt. 69° C.
Phenyl*cyclo*hexane	$C_{12}H_{16}$	160	3·681	2·377	1·380	0·955	0·762	,,	
Di*cyclo*hexyl	$C_{12}H_{22}$	166	7·413	4·027	1·995	1·279	0·982	,,	
Dibenzyl	$C_{14}H_{14}$	182	—	(4·624)	2·198	1·387	1·064	,,	M. pt. 52·5° C.
Di*cyclo*hexylethane	$C_{14}H_{26}$	194	17·99	8·128	3·266	1·901	1·409	,,	
Hexylnaphthalene (26)	$C_{16}H_{20}$	212	23·93	8·84	3·28	1·73	1·26	Mikeska	
Dihydrodiethylanthracene	$C_{18}H_{20}$	236	—	157·0	17·30	5·176	—	Lerer	
Di*iso*butylnaphthalene	$C_{18}H_{24}$	240	—	47·21	8·511	3·420	(2·249)	,,	
1 : 2 : 3 : 4-Tetrahydro-1 : 4-di*iso*-butylnaphthalene	$C_{18}H_{28}$	244	—	40·30	8·630	3·420	—	,,	
Dihexylnaphthalene (27)	$C_{22}H_{32}$	296	155·3	42·0	11·16	4·63	2·95	Mikeska	
Dihydrodi*iso*amylanthracene	$C_{24}H_{32}$	320	—	4920	184·5	23·66	—	Lerer	
1 : 1-Diphenylhexadecene-1	$C_{28}H_{40}$	376	164·9	46·8	13·1	5·56	3·70	Landa and Čech	
1 : 1-Diphenylhexadecane	$C_{28}H_{42}$	378	166·3	47·4	13·1	5·55	3·68	,, ,,	
Trihexylnaphthalene (28)	$C_{28}H_{44}$	380	305·8	75·4	18·18	6·97	4·32	Mikeska	
Trihexylnaphthalene (29)	$C_{28}H_{44}$	380	434·3	100·2	22·65	8·33	5·04	,,	
Octadecylnaphthalene (15)	$C_{28}H_{44}$	380	124·5	42·5	13·35	5·96	3·92	,,	M. pt. 51–52° C.
Octadecyltetrahydronaphthalene (31)	$C_{28}H_{48}$	384	124·1	42·6	13·55	6·08	4·02	,,	M. pt. 29–30° C.
1 : 1-Di*cyclo*hexylhexadecane	$C_{28}H_{54}$	390	275·4	70·8	17·3	6·86	4·35	Landa and Čech	
Octadecyldecahydronaphthalene (37)	$C_{28}H_{54}$	390	154·6	52·0	16·35	7·21	4·70	Mikeska	M. pt. 43–47° C.
5 : 14-Diphenyloctadecadiene-5, 13 (50)	$C_{30}H_{42}$	402	254	64·4	15·6	6·18	3·98	,,	
1 : 1-Diphenyloctadecene-1 (47)	$C_{30}H_{44}$	404	211·1	59·45	16·08	6·53	4·14	,,	
Dihydro-di-β-octylanthracene	$C_{30}H_{44}$	404	—	1476	115·1	(24·75)	—	Lerer	
1-Phenyl-2-benzylheptadecene-2	$C_{30}H_{44}$	404	430·5	78·5	17·06	6·70	4·28	Landa and Čech	
1 : 1-Diphenyloctadecane (48)	$C_{30}H_{46}$	406	165·6	55·75	15·2	6·31	4·02	Mikeska	
5 : 14-Diphenyloctadecane (51)	$C_{30}H_{46}$	406	336	77·2	17·7	6·71	4·18	,,	
Octadecyldiphenyl (40)	$C_{30}H_{46}$	406	182	57·2	16·8	7·15	4·61	,,	M. pt. 77·5–78° C.
1-Phenyl-2-benzylheptadecane	$C_{30}H_{46}$	406	380·2	81·5	18·4	6·92	4·35	Landa and Čech	
1-*cyclo*Hexyl-2-hexahydrobenzyl-									

1 : 1-Diphenyloctadecene-1 (47)	$C_{30}H_{44}$	404	211·1	59·45	16·08	6·53	4·14	,,	
Dihydro-di-β-octylanthracene	$C_{30}H_{44}$	404	—	1476	115·1	(24·75)	—	Lerer	
1-Phenyl-2-benzylheptadecene-2	$C_{30}H_{44}$	404	430–5	78·5	17·06	6·70	4·28	Landa and Čech	
1 : 1-Diphenyloctadecane (48)	$C_{30}H_{46}$	406	195·6	55·75	15·2	6·31	4·62	Mikeska	
5 : 14-Diphenyloctadecane (51)	$C_{30}H_{46}$	406	336	77·2	17·7	6·71	4·18	,,	
Octadecyldiphenyl (40)	$C_{30}H_{46}$	406	182	57·2	16·8	7·15	4·61	,,	M. pt. 77·5–78° C.
1-Phenyl-2-benzylheptadecane	$C_{30}H_{46}$	406	380·2	81·5	18·4	6·92	4·35	Landa and Čech	
1-*cyclo*Hexyl-2-hexahydrobenzyl-heptadecane	$C_{30}H_{58}$	418	242·3	64·0	16·3	6·52	4·17	,, ,,	
(1-Butyloctadecen-1-yl)naphthalene (18)	$C_{32}H_{50}$	434	233·6	65·6	17·5	7·08	4·44	Mikeska	
Docosylnaphthalene (16)	$C_{32}H_{52}$	436	217	69·3	20·3	8·54	5·45	,,	M. pt. 56–58° C.
(1-Butyloctadecyl)naphthalene (17)	$C_{32}H_{52}$	436	269·5	74·8	19·6	7·78	4·49	,,	
(1-Butyloctadecen-1-yl)tetrahydronaphthalene (34)	$C_{32}H_{54}$	438	411·8	103·6	25·2	9·51	5·83	,,	
Docosyltetrahydronaphthalene (32)	$C_{32}H_{56}$	440	214	68·9	20·7	8·76	5·63	,,	M. pt. 42–45° C.
(1-Butyloctadecyl)tetrahydronaphthalene (33)	$C_{32}H_{56}$	440	511·2	119·3	26·8	9·64	5·73	,,	
Docosyldecahydronaphthalene (38)	$C_{32}H_{62}$	446	260	81·4	23·6	9·78	6·20	,,	
1-Butyloctadecyldecahydronaphthalene (39)	$C_{32}H_{62}$	446	416·6	109·8	26·55	10·01	6·07	,,	
1-Phenyl-1-naphthyloctadecene-1 (49)	$C_{34}H_{46}$	454	1502	260·6	44·8	13·87	7·77	,,	
(1-Butyloctadecen-1-yl)diphenyl (41)	$C_{34}H_{52}$	460	463	117	27·9	10·4	6·30	,,	M. pt. 47–48° C.
(1-Butyloctadecyl)diphenyl (42)	$C_{34}H_{54}$	462	530·3	129·0	29·5	10·64	6·37	,,	M. pt. 41·5–43° C.
Docosyldiphenyl (43)	$C_{34}H_{54}$	462	248·7	77·2	21·9	9·15	5·84	,,	M. pt. 82–84·5° C.
(2-Butyleicosyl)naphthalene (21)	$C_{34}H_{56}$	464	306	85·7	22·8	9·00	5·63	,,	
(1-Butyloctadecyl)diphenyl (46)	$C_{34}H_{66}$	474	865·8	183·6	28·85	12·55	7·27	,,	
(1-Ethyl-2-butyleicosen-1-yl)-naphthalene (22)	$C_{36}H_{58}$	478	597	140·3	29·9	10·8	6·50	,,	
(1-Butyldocosen-1-yl)naphthalene (20)	$C_{36}H_{58}$	490	247·2	74·4	20·65	8·48	5·35	,,	
(1-Butyldocosyl)naphthalene (19)	$C_{36}H_{60}$	492	278·3	80·7	21·8	8·77	5·51	,,	M. pt. 39–40° C.
(1-Ethyl-2-butyleicosyl)naphthalene (25)	$C_{36}H_{60}$	492	696·5	155·2	32·8	11·4	6·68	,,	
(1-Butyldocosen-1-yl)tetrahydronaphthalene (35)	$C_{36}H_{62}$	494	554·6	137·6	31·3	11·6	6·99	,,	
(1-Butyldocosyl)tetrahydronaphthalene (36)	$C_{36}H_{64}$	496	594·8	146·9	33·8	12·35	7·37	,,	M. pt. 35° C.
(1-Butyldocosen-1-yl)diphenyl (44)	$C_{38}H_{60}$	516	607	149·5	35·4	12·9	7·76	,,	M. pt. 37–39° C.
(1-Butyldocosyl)diphenyl (45)	$C_{38}H_{62}$	518	704·2	170·3	38·05	13·6	7·97	,,	M. pt. 44–45° C.
(1 : 2-Dibutyleicosen-1-yl)naphthalene (24)	$C_{38}H_{62}$	518	633·4	146·4	32·3	11·4	6·79	,,	
(1 : 2-Dibutyleicosyl)naphthalene (23)	$C_{38}H_{64}$	520	789·3	170·9	35·05	12·0	7·03	,,	

Note.—Numbers following names of hydrocarbons refer to those in Mikeska's paper.

TABLE XLVI.

Hydrocarbon.	d_4^0.	d_4^{50}.	d_4^{100}.	0° C.	20° C.	50° C.	80° C.	100° C.
Indene	1·0152	0·9692	0·9232	2·895	1·820	1·085	0·7800	0·644
Hydrindene	0·9813	0·9378	0·8942	2·280	1·550	0·9790	0·7280	0·6060
Naphthalene	1·0373	0·9991	0·9609	—	2·430	1·423	0·9875	0·7920
1 : 2 : 3 : 4-Tetrahydronaphthalene	0·9866	0·9469	0·9072	3·655	2·300	1·325	0·9395	0·7695
Decahydronaphthalene	0·8982	0·8609	0·8236	4·640	2·980	1·705	1·180	0·9490
Dicyclopentyl	0·8761	0·8389	0·8017	2·195	1·630	1·095	0·8295	0·6985
α-Methylnaphthalene	1·0347	0·9979	0·9611	5·900	3·270	1·680	1·130	0·9020
β-Methylnaphthalene	1·0562	0·9960	0·9357	—	2·485	1·365	0·9480	0·7705
Phenylcyclopentane	0·9618	0·9228	0·8838	2·775	1·880	1·175	0·8730	0·7320
cycloHexylcyclopentane	0·8907	0·8535	0·8163	5·215	3·110	1·720	1·190	0·9555
Diphenyl	1·0502	1·0096	0·9690	—	3·610	1·940	1·270	0·9900
Phenylcyclohexane	0·9591	0·9183	0·8775	3·840	2·520	1·505	1·070	0·8685
Dicyclohexyl	0·8988	0·8638	0·8288	8·245	4·550	2·310	1·520	1·185
Dibenzyl	1·0027	0·9655	0·9283	—	4·680	2·275	1·470	1·145
Dicyclohexylethane	0·8893	0·8560	0·8227	20·23	9·280	3·815	2·275	1·710
Hexylnaphthalene (26)	0·9730	0·9420	0·9110	24·6	9·20	3·48	1·87	1·38
Dihydrodiethylanthracene	1·0264	0·9949	0·9634	—	154·8	17·39	5·305	—
Diisobutylnaphthalene	0·9424	0·9104	0·8784	—	50·78	9·350	3·835	2·560
1 : 2 : 3 : 4-Tetrahydro-1 : 4-diisobutylnaphthalene	0·9259	0·8939	0·8619	—	44·15	9·655	3·910	—
Dihexylnaphthalene (27)	0·9477	0·9152	0·8847	164	45·0	12·2	5·16	3·33
Dihydrodiisoamylanthracene	0·9868	0·9499	0·9130	—	5062	194·2	25·60	—
1 : 1-Diphenylhexadecene-1	0·9316	0·8991	0·8666	177·0	50·9	14·6	6·32	4·27
1 : 1-Diphenylhexadecane	0·9265	0·8940	0·8615	179·6	51·9	14·6	6·34	4·27
Trihexylnaphthalene (28)	0·9267	0·8952	0·8637	330	82·5	20·3	7·96	5·0
Trihexylnaphthalene (29)	0·9240	0·8920	0·8600	470	110	25·4	9·54	5·86
Octadecylnaphthalene (15)	0·9223	0·8897	0·8571	135	46·7	15·0	6·85	4·57
Octadecyltetrahydronaphthalene (31)	0·8989	0·8691	0·8393	138	48·0	15·6	7·14	4·79
1 : 1-Dicyclohexylhexadecane	0·8921	0·8596	0·8271	308·7	80·5	20·2	8·16	5·13
Octadecyldecahydronaphthalene (37)	0·8785	0·8475	0·8168	176	60·0	19·3	8·7	5·76
5 : 14-Diphenyloctadecadiene-5, 13 (50)	0·9461	0·9151	0·8841	269	69·0	17·0	6·9	4·5
1 : 1-Diphenyloctadecane-1 (47)	0·9465	0·9140	0·8815	223	63·7	17·6	7·3	4·7
Dihydrodi-β-octylanthracene	0·9646	0·9331	0·9016	—	1550	123·4	27·10	—
1-Phenyl-2-benzylheptadecene-2	0·9367	0·9042	0·8717	459·6	85·0	18·9	7·57	4·92
1 : 1-Diphenyloctadecane (48)	0·9420	0·9100	0·8780	207	60	16·7	7·08	4·58
5 : 14-Diphenyloctadecane (51)	0·9206	0·8896	0·8586	365	85	19·9	7·7	4·87
Octadecyldiphenyl (40)	0·9278	0·8968	0·8658	196	62·5	18·7	8·14	5·33
1-Phenyl-2-benzylheptadecane	0·9296	0·8969	0·8642	409·0	88·9	20·5	7·89	5·03
5 : 14-Dicyclohexyloctadecane (52)	—	—	—	690	142	28·9	10·4	6·3
1-cycloHexyl-2-hexahydrobenzylheptadecane	0·8990	0·8665	0·8340	269·5	72·25	18·8	7·70	5·00
(1-Butyloctadecen-1-yl)-naphthalene (18)	0·9236	0·8926	0·8616	253	72	19·6	8·1	5·15
Docosylnaphthalene (16)	0·9121	0·8811	0·8501	238	77	23·0	9·9	6·41
(1-Butyloctadecyl)naphthalene (17)	0·9132	0·8827	0·8522	295	83	22·2	9·0	5·27
(1-Butyloctadecen-1-yl)tetrahydronaphthalene (34)	0·9053	0·8748	0·8443	455	116	28·8	11·1	6·9
Docosyltetrahydronaphthalene (32)	0·8959	0·8649	0·8339	239	78	23·9	10·35	6·75
(1-Butyloctadecyl)tetrahydronaphthalene (33)	0·8970	0·8650	0·8330	570	135	31	11·4	6·88
Docosyldecahydronaphthalene (38)	0·8783	0·8473	0·8163	296	94	27·8	11·8	7·6
1-Butyloctadecyldecahydronaphthalene (39)	0·8770	0·8460	0·8150	475	127	31·4	12·1	7·45
1-Phenyl-1-naphthyloctadecene-1 (49)	0·9628	0·9333	0·9038	1560	274	48	15·1	8·6
(1-Butyloctadecen-1-yl)diphenyl (41)	0·9258	0·8948	0·8638	500	128	31·2	11·9	7·3
(1-Butyloctadecyl)diphenyl (42)	0·9145	0·8836	0·8527	580	143	33·4	12·3	7·47
Docosyldiphenyl (43)	0·9210	0·8900	0·8590	270	85	24·6	10·5	6·8
(2-Butyleicosyl)naphthalene (21)	0·9149	0·8839	0·8529	335	95	25·8	10·4	6·6
(1-Butyloctadecyl)diphenyl (46)	0·8835	0·8505	0·8175	980	211	33·9	15·1	8·90
(1-Ethyl-2-butyleicosen-1-yl)-naphthalene (22)	0·9115	0·8805	0·8495	655	156	33·9	12·5	7·65
(1-Butyldocosen-1-yl)naphthalene (20)	0·8988	0·8673	0·8358	275	84	23·8	10·0	6·4
(1-Butyldocosyl)naphthalene (19)	0·8947	0·8637	0·8327	311	91·5	25·2	10·4	6·62

TABLE XLVI.—*Continued.*

Hydrocarbon.	d_4^0.	d_4^{50}.	d_4^{100}.	0° C.	20° C.	50° C.	80° C.	100° C.
(1-Ethyl-2-butyleicosyl)naphthalene (25) . .	0·9045	0·8735	0·8425	770	174	37·5	13·3	7·95
(1-Butyldocosen-1-yl)tetrahydronaphthalene (35) .	0·8945	0·8635	0·8325	620	156	36·2	13·7	8·4
(1-Butyldocosyl)tetrahydronaphthalene (36) . .	0·8919	0·8604	0·8289	667	167	39·3	14·7	8·90
(1-Butyldocosen-1-yl)diphenyl (44)	0·9345	0·9035	0·8725	650	162	39·2	14·6	8·9
(1-Butyldocosyl)diphenyl (45).	0·9086	0·8782	0·8478	775	190	43·3	15·8	9·4
(1 : 2-Dibutyleicosen-1-yl)-naphthalene (24) . .	0·9051	0·8741	0·8431	700	164	37	13·3	8·05
(1 : 2-Dibutyleicosyl)naphthalene (23)	0·9073	0·8763	0·8453	870	191	40	14·0	8·32

Note.—Numbers following names of hydrocarbons refer to those in Mikeska's paper.

25° C. and in these cases the coefficient of 0·00062 per degree Centigrade has been used for the change of density with temperature. The values at 25° C. for hydrocarbons 11 * and 45 should be 0·8277 and 0·8935 respectively. For compounds 16, 21, 32, 38, 40, 41, 43 and 44 unusual coefficients are obtained, and in the absence of obvious reasons for these divergencies it has been considered advisable to employ the coefficient 0·00062.

Tables XLI–XLIV contain the original data and Tables XLV and XLVI the summarized data in centipoises and centistokes respectively.

Preparation and Properties of Hydrocarbons.

Indene.—Pure indene was obtained by the careful fractionation of a purchased sample. The properties were as follows: b.pt., corr., 181·8–182·3° C.; d_4^{20} 0·9968; d_4^{50} 0·9692; n_D^{15} 1·5790; n_D^{20} 1·5768. There is not much data in the literature on the properties of indene, and these are rather variable. For instance, the I.C.T. give 1·006 for the density at 20° C., Cortese [60] gives a value at 25° C., which corresponds with 0·989 at 20° C. Data on the refractive index also vary; the I.C.T. figure is 1·571 at 20° C., whilst Zelinski and Turova-Pollak [61] give 1·5769, which is in fair agreement with our own figure.

Hydrindene.—Indene hydrogenates very readily, under the conditions previously described, to give hydrindene, the reaction being complete in less than an hour. After fractionation the physical properties were determined: b.pt., corr., 177·5–178·5° C.; d_4^{20} 0·9639; d_4^{50} 0·9378; n_D^{15} 1·5407; n_D^{20} 1·5383. The I.C.T. give b.pt. 176·5°; density 0·965 at 20° C. and $n_D^{21·4}$ 1·5370.

Naphthalene.—The naphthalene used was B.D.H. "extra pure for molecular weight determinations," and was used without further purification. The m.pt. was 80·5° C., which agrees with the best determinations in the literature. The material gave an iodine number of 2·3 by the Hanus method and 0·4 by the Wijs method, showing that slight substitution occurred in the former method; this is probably due to slight excess of free bromine in the reagent. The only other constants determined were the densities at 90° C. and 120° C., which were 0·9685 and 0·9456 respectively.

* Hydrocarbon No. 11 is discussed in Part V, on the Monocyclic Naphthenes.

1-*Methylnaphthalene*.—The starting material in this case was the product used as a reference standard in the evaluation of diesel-engine fuels. The separation of 1- and 2-methylnaphthalenes is a matter of some difficulty. The properties of the starting material (*e.g.*, $n_D^{20} = 1{\cdot}617$) indicated that it was probably very pure 1-methylnaphthalene. Initial experiments involving sulphonation and fractional steam distillation of the sulphonic acids did not give very promising results, so it was next attempted to purify the substance by fractional crystallization of the picrate, 50 g. of the methylnaphthalene being converted to picrate by mixing the acetone solutions of the reagents, and fractionally precipitating with water. Finally three main fractions were obtained which were recrystallized from alcohol. Each of these fractions melted fairly sharply at 140–141° C., which is the figure given by Baril and Hauber [62] for the α-picrate, the β-picrate melting at 115–116° C. Decomposition of the picrates with sodium hydroxide gave fractions with n_D^{20} of 1·6172 for the material derived from the least soluble picrate, 1·6170 for the middle fraction and 1·6065 for that from the most soluble picrate. There is thus little evidence of separation, so that either there is little or no β-methylnaphthalene present, or crystallization of the picrates does not afford a method of separation. Morgan and Coulson,[63] in a paper published subsequent to this work, reached the conclusion that fractionation of the picrates did not lead to separation, and adopted a method depending on the different solubilities of the sulphonic acids in 50 per cent. sulphuric acid. This method was not available at the time, and it was decided to rely on careful fractionation of the material. True, there is only about 2° C. difference in the boiling points, but it was considered established that the amount of β-isomer present was very small, and as a large quantity of the material was available, careful fractionation seemed the best method of attack. The lowest figure obtained for n_D^{20} on any fraction was 1·6150, the residue showed 1·6177 and the best fraction had n_D^{20} 1·6172. The properties of this material were: b.pt., corr., 244·4° C. (const.); d_4^{20} 1·020; d_4^{30} 0·9979; n_D^{15} 1·6197; n_D^{20} 1·6172; n_D^{25} 1·6145; m.pt. − 31° C.; m.pt., picrate, 141° C. (sharp); iodine number (Wijs) 0·25. Data in the literature are generally untrustworthy; the I.C.T. give −22° C. for the m.pt., Morgan and Coulson (*loc. cit.*) give m.pt. −33° C. to −32° C. and b.pt. 238–240° C. for a sample isolated from low-temperature tar, and 139–140° C. for the m.pt. of the pure picrate.

2-*Methylnaphthalene*.—2-Methylnaphthalene purchased from the B.D.H. was recrystallized from alcohol until no further change in melting point occurred. The highest figure thus obtained was 34·5° C. The other properties derermined were: d_D^{40} 1·008; d_D^{70} 0·9718; n_D^{40} 1·6015; n_D^{50} 1·5965. The I.C.T. figures are d_4^{20} 1·029; n_D^{40} 1·6026; m.pt. 35·1° C. (d_4^{20} calculated from our results is about 1·032). In this case also the figures in the literature are very varied—*e.g.*, m.pts. from 32° C. to 37–38° C. are recorded.

Tetralin (1 : 2 : 3 : 4-*Tetrahydronaphthalene*).—The commercially obtainable product was purified by treatment with 60 per cent. sulphuric acid and refractionation over sodium. (The main impurities are likely to be either unchanged naphthalene or decalin, the former of which has a higher and the latter a lower boiling point.) The following physical constants were obtained: b.pt. 206·6–207·0° C.; d_4^{20} 0·9707; d_4^{50} 0·9469; n_D^{15} 1·5465;

n_D^{20} 1·5438. The I.C.T. figures are: d_4^{20} 0·971; b.pt. 207·2° C.; $n_D^{17\cdot8}$ 1·5451; which are in excellent agreement.

Decalin (*Decahydronaphthalene*) is a mixture of *cis*- and *trans*-isomers. It was not attempted to separate these, but the material was purified by treatment with 99 per cent. sulphuric acid and distillation. From the constants of the product it is seen to be a mixture of approximately 40–45 per cent. of the *cis*-isomer and 60–55 per cent. of the *trans*-isomer.

	B. pt.	d_4^{20}.	d_4^{50}.	n_D^{15}.	n_D^{20}.	A. pt.
Our sample . .	191·6 ± 1·0	0·8833	0·8609	1·4773	1·4750	35·3
cis-Isomer (I.C.T.) .	193·3	0·898	—	—	1·4828	—
trans-Isomer (I.C.T.) .	185·3	0·872	—	—	1·4701	—

Diphenyl.—This compound can be bought in a very pure condition, and it was only necessary to recrystallize from alcohol. The physical properties determined were: m.pt. 69·8° C.; d_4^{75} 0·9893; d_4^{105} 0·9649; the I.C.T. figures being m.pt. 69·0° C.; d_4^{20} 1·041. Fittig [64] gives 70·5° C. as the melting point of diphenyl.

Dibenzyl.—This hydrocarbon was obtained as a by-product in the preparation of *n*-butylbenzene by the method of Radziswewski (*loc. cit.*), which consists of refluxing benzyl chloride with propyl bromide and sodium. The residues, after fractionation to remove butylbenzene, contained a large quantity of dibenzyl, which was recovered by dissolving in alcohol and boiling with animal charcoal to remove the colouring matter. Repeated treatment in this way and recrystallization from alcohol gave a solid, m.pt. 53·0° C., almost pure white in colour and with d_4^{60} 0·9581 and d_4^{80} 0·9358. The I.C.T. figures are m.pt. 52·5° C. and $d_4^{80\cdot6}$ 0·942, which are in fairly good agreement.

Dicyclopentyl.—*cyclo*Pentyl bromide was obtained by the action of gaseous hydrogen bromide on *cyclo*pentanol. 75 g. of the bromide were dissolved in ether and added slowly to 20 g. sodium covered with 250 ml. ether. A gentle action started, and the mixture was left 24 hours under reflux. The ether solution was filtered and fresh sodium added, after which the ether was distilled off and the di*cyclo*pentyl distilled over sodium. The yield of pure hydrocarbon in several experiments was 20–25 per cent. Di*cyclo*pentyl is a pleasant-smelling liquid with the following physical properties: b.pt., corr., 189–191° C.; d_4^{20} 0·8612; d_4^{50} 0·8389; n_D^{15} 1·4660; n_D^{20} 1·4638; a.pt. 35·8° C. Zelinsky, Titz and Fataiev [65] record, b.pt. 188–189° C. at 753 mm., d_4^{20} 0·8604; n_D^{20} 1·4652; whilst Meiser [66] obtained 189–191° C. for the boiling point.

Dicyclohexyl.—It was first attempted to prepare this hydrocarbon by the action of sodium on *cyclo*hexyl chloride, but the yield was very poor, *cyclo*hexene being the main product. Hydrogenation of diphenyl was then tried, but only about 10 per cent. of the material was hydrogenated after about twenty hours' shaking, using three successive portions of catalyst. Finally the action of sodium on *cyclo*hexyl bromide was employed, the reaction being carried out very slowly by adding the bromide in ethereal solution to sodium covered in ether, during the course of a day, then boiling gently for some hours and distilling off the ether. Fractionation over

sodium finally yielded a pure product, but the yield was only about 20 per cent. B.pt., corr., 238–239° C.; d_4^{20} 0·8848; d_4^{50} 0·8638; n_D^{15} 1·4817; n_D^{20} 1·4795; a.pt. 47·5° C. Zelinsky, Titz and Fataiev [67] obtained, b.pt. 239·5° C.; d_4^{20} 0·8847; n_D^{20} 1·4800.

*Phenyl*cyclo*pentane*.—This was prepared in 70 per cent. yield by the Friedel–Craft's reaction, using *cyclo*pentyl chloride, benzene and aluminium chloride. It was a pleasant-smelling liquid, with a rose-like odour, with b.pt., corr., 219·5–220·5° C.; d_4^{20} 0·9462; d_4^{50} 0·9228; n_4^{15} 1·5301; n_D^{20} 1·5280. Zelinsky and Titz [68] claimed a 54 per cent. yield with b.pt. 217° C.; d_4^{20} 0·9474; and n_D^{20} 1·5280.

*Phenyl*cyclo*hexane*.—In this case also the Friedel–Craft's reaction was employed, using *cyclo*hexyl chloride, benzene and aluminium chloride. The yield was 40 per cent. the physical properties being: b.pt., corr., 239·0 ± 0·6° C.; d_4^{20} 0·9428; d_4^{50} 0·9183; n_D^{15} 1·5288; n_D^{20} 1·5260. Bodroux [69] gives b.pt. 238–240° C. at 743 mm.; d_{16} 0·947; n_D^{16} 1·528.

cyclo*Hexyl*cyclo*pentane*.—Phenyl*cyclo*pentane hydrogenates fairly easily in acetic acid solution in the presence of platinum black. Under the conditions previously described, the reaction was completed in 6 hours or less. The separated hydrocarbon was treated with sulphuric acid, washed and distilled; b.pt., corr., 215·5 ± 0·5° C.; d_4^{20} 0·8758; d_4^{50} 0·8535; n_D^{15} 1·4749; n_D^{20} 1·4728; a.pt. 42·5° C. Zelinsky and Titz [70] recorded, b.pt. 214° C.; d_4^{21} 0·8780; n_D^{21} 1·4728.

*Di*cyclo*hexylethane*.—Dibenzyl hydrogenates fairly well under the conditions used, about 60 per cent. of the compound being converted to di*cyclo*hexylethane after about 24 hours' shaking.

The mono-alkylbenzenes hydrogenate comparatively easily in acetic acid solution in the presence of platinum black, to give the corresponding *cyclo*hexane derivatives. Diphenyl is very difficult to hydrogenate by this means, but phenyl*cyclo*pentane is quite easily reduced and probably phenyl*cyclo*hexane would also react easily; probably this latter reaction would be the best means of preparing di*cyclo*hexyl. The steric effect of two phenyl groups joined directly is apparently to make the compound very resistant to hydrogenation. Increasing the distance between the benzene nuclei renders the hydrogenation more easy, as is shown by the fairly ready hydrogenation of dibenzyl.

The hydrocarbon remaining after 24 hours' treatment of dibenzyl was separated with water from acetic acid solution, and the product sulphonated to remove unchanged dibenzyl. The di*cyclo*hexylethane was distilled and then showed the following physical constants: b.pt., corr., 273° C.; d_4^{20} 0·8760; d_4^{50} 0·8560; n_D^{15} 1·4790; a.pt. 61·0° C. The only previous data appear to be those of Adams and Marshall,[71] who give: b.pt. 147–148·5° C./12 mm.; d_4^{18} 0·8774; n_D^{18} 1·4760; which are in fairly good agreement.

Parts III–VIII contain the collected and summarized data on the viscosities of hydrocarbons. The final tables have been compiled after critical evaluation of the data, but it has not been possible, in a limited space, to deal fully with all the details involved in the selection of the data.

It is almost inevitable that, in the large amount of data here collated, some inaccuracies will be found. The author will be grateful if such of these as may be noted are brought to his attention.

Errata, Part III.

The figures for the viscosities of *n*-decane at 80° C. should be 0·430 cp. and 0·629 cs. respectively in Tables XI and XII.

Errata, Part V.

In Table XXII octadecyl*cyclo*hexane should be followed by the bracketed number (11) and not by (1).

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PHYSICAL AND CHEMICAL CONSTANTS OF NORMAL PARAFFINS.*

By D. J. W. Kreulen (Member).

In the work of Leendertse, Vlugter, Waterman and van Westen,[1] the constitution of the oil molecule is calculated from the deviations of the physical and chemical constants of the completely hydrogenated oil sample, from the figures accepted for known oil structures, such as normal paraffins, monocyclic naphthenes, etc.

There is a considerable amount of data in the literature concerning these constants, although the agreement between the figures given by different authors is rather poor. Moreover, only rarely are series of homologues of different molecular weight investigated, and even then only a few constants are recorded.

Consequently, even from a standard work such as "The Science of Petroleum" it is not possible to gather all the figures presented in this paper. Yet an exact knowledge of such data is of the utmost importance if we wish to place future considerations on a reliable basis. Now, it is true that Waterman and his co-workers tested their methods on a large number of substances of known constitution and found them completely reliable. It could therefore be expected that we, too, should find figures, both for the specific refraction and for the specific parachor, which would correspond with those theoretically calculated from the atomic refractions (Eisenlohr) and the atomic parachors (Mumford and Phillips).

This proved to be the case, showing at the same time—since we worked with mixtures—the sufficient additional character of the figures.

Preparation of the Series of Paraffins.

In our experiments we started with Borneo paraffin obtained from the B.I.M. This paraffin was cracked by us for different periods of time in the presence of hydrogen (initial pressure about 270 atm.) at 440° C., Ni being used as a catalyst. Care was taken that no cyclization occurred (controlled by the specific dispersion method). In this case the paraffin was not coloured after treatment and did not show any fluorescence. Samples of different molecular weight were obtained from the cracked paraffin either by carefully heating to remove the lower members of the series, or by fractional crystallization at successive temperatures. At last a liquid residue was obtained which was separated into fractions by careful distillation. Heating with an open flame was always avoided.

Methods of Analysis.

For the methods of analysis, reference may be made to a preceding paper.[2] The density was determined at at least three different tem-

* Paper received June 15th, 1938.

peratures spreading over 20° C. Although great accuracy was attained, on account of the extrapolation, the results are considered to be reliable within 0·0005 unit.

In the same way the refraction N_{20}^{D} was obtained. The determinations of this constant, however, comprised greater difficulties than the determination of the density. For this reason ten refraction as well as ten dispersion readings were taken by two independent observers, and the average of the readings was taken. A straight-line graph was required. The extrapolated 20° C. values are considered to be reliable within 0·0010 unit.

With regard to the aniline point, it should be mentioned that all the samples, in a molten state, were carefully dried with heated calcium chloride before testing. Equal volumes of aniline and paraffin were then brought together. This was effected by weighing, due consideration being given to the densities. The accuracy of the lower results is of the order of 0·2° C., that of the higher figures of the order of 0·4° C.

The viscosity was determined by means of the Vogel–Ossag viscosimeter. No experiments were carried out at temperatures less than 10° C. above the temperature at which a cloud could be observed. The same capillary (constant = 0·0158) was used for all the determinations. The results, obtained at different temperatures, fell on a straight line if plotted against temperature, according to the well-known Ubbelohde relationship.

The surface tension was measured by Jeager's method modified by Nellensteyn. It was determined at different temperatures, and the 20° C. values were extrapolated from the straight lines. Depending on certain experimental difficulties (such as crystallization phenomena in the testing capillary at lower temperatures), the 20° C. values are considered to be reliable to within 0·5 dyne/cm.

Results of Analysis.

The results obtained were plotted graphically against molecular weight. The average curves were then drawn, and from these curves the most probable figures were read off for every increase in molecular weight of 50 units. The results obtained for the samples and those read from the graphs are collected in the following tables. The graphs are also given. From these graphs one can judge the position of the determined figures relative to the resulting average curve.

Discussion of Results.

The most important results obtained in this investigation are the graphs, most of which do not require any further discussion. From the graphs it is evident, if we compare the results with the theoretical values, that we were dealing with a series of normal paraffins. If any branching of the hydrocarbon chains exists, this branching is practically nil, so that we have to regard the constants obtained as being those of normal paraffins.

There is a certain tendency to obtain a lower surface tension than that which is calculated theoretically from the atomic parachors of Mumford and Phillips. It is quite possible that experimental difficulties are here

TABLE I.

Results of Samples.

Mean Mol. Weight.	Density 20/4.	Δ Density.	N_D^{20}.	$\frac{(N_{g'} - N_c)10^4}{d}$.	Aniline Point, ° C.	Surface Tension, dyne/cm.
498	—	—	—	—	127·2	—
481	0·8131	0·000643	1·4560	158	126·9	31·50
420	0·8076	0·000657	1·4528	156	121·4	30·28
338	0·7975	0·000667	1·4466	156	116·7	29·52
302	0·7923	0·000665	1·4432	157	112·1	28·91
247	0·7800	0·000684	1·4362	158	104·6	27·89
224	0·7720	0·000699	1·4338	157	95·8	26·90
207	0·7696	0·000699	1·4332	158	97·8	26·89
206	0·7664	0·000708	1·4313	157	94·8	26·53
138	0·7281	0·000774	1·4111	158	77·5	23·51
		Average Results Read from Graphs.				
500	0·8143	0·000646	1·4558	—	127·7	—
450	0·8103	0·000650	1·4535	—	124·8	30·58
400	0·8053	0·000655	1·4507	—	121·2	30·14
350	0·7998	0·000661	1·4475	—	117·2	29·60
300	0·7918	0·000670	1·4434	—	112·2	28·93
250	0·7809	0·000684	1·4378	—	104·3	27·94
200	0·7635	0·000710	1·4292	—	93·2	26·41
150	0·7353	0·000759	1·4153	—	80·5	24·19
100	—	—	—	—	68·0	—

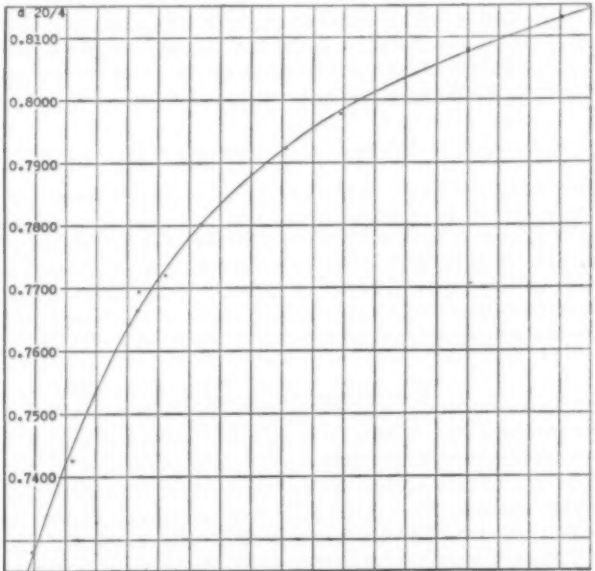

FIG. 1.

DENSITY PLOTTED AGAINST MOLECULAR WEIGHT.

involved. In each case, however, these deviations are not serious, as we calculate from them 0·6 to 1·3 extra tertiary carbon atoms.

TABLE II.

*Results of Samples.**

Mean Mol. Weight.	Viscosity c. st. 20° C.	W 20° C.	Viscosity c. st. 50° C.	W 50° C.	m.	W_p.
481	39·30	+0·2050	14·52	+0·0738	3·10	0·38
420	25·31	+0·1513	10·25	+0·0184	3·14	0·33
338	16·94	+0·0966	7·31	−0·0414	3·26	0·28
302	11·69	+0·0400	5·49	−0·0980	3·26	0·23
247	6·38	−0·0675	3·44	−0·2030	3·20	0·11
224	4·22	−0·1546	2·30	−0·3083	3·63	0·05
207	4·18	−0·1564	2·34	−0·3033	3·47	0·04
206	3·62	−0·1897	2·06	−0·3391	3·53	0·01

* W being log log (ν + 0·8); m the coefficient of direction of the equation $W = m(\log T_1 - \log T) + W_1$, and W_p the "viscosity pole" of Ubbelohde given by $W_p = \frac{1}{\frac{1}{m} - 0{\cdot}194}(0{\cdot}0992 + \frac{1}{m} \cdot W_{50°})$.

TABLE III.

Mean Mol. Weight.	Specific Refraction.			Specific Parachor.		
	A.	*A*1.	*A*2.	*B*.	*B*1.	*B*2.
481	0·3343	0·3337	0·3328	2·914	2·898	2·904
420	0·3345	0·3338	0·3332	2·905	2·905	2·913
338	0·3348	0·3345	0·3339	2·923	2·919	2·927
302	0·3347	0·3350	0·3344	2·927	2·928	2·936
247	0·3354	0·3362	0·3356	2·946	2·946	2·954
224	0·3372	0·3368	0·3362	2·950	2·956	2·965
207	0·3378	0·3376	0·3367	2·959	2·965	2·974
206	0·3379	0·3377	0·3368	2·961	2·966	2·975
138	0·3411	0·3412	0·3405	3·024	3·029	3·036

A and *B* = results of samples.
*A*1 and *B*1 = results calculated from average figures read from the graphs (see Table I).
*A*2 = theoretical figure derived from the atomic refractions according to Eisenlohr.
*B*2 = theoretical figure derived from the atomic parachors according to Mumford and Phillips.

According to Waterman and Leendertse, an accuracy of 1–2 extra tertiary carbon atoms for a molecular weight < 200, and 3–4 extra tertiary carbon atoms for a molecular weight from 400 to 600 is sufficient. The results obtained in our case must, therefore, be considered as quite satisfactory.

The temperature–surface-tension relationship was found to be on an average 0·066 dyne/cm. ° C. (max. 0·079; min. 0·054).

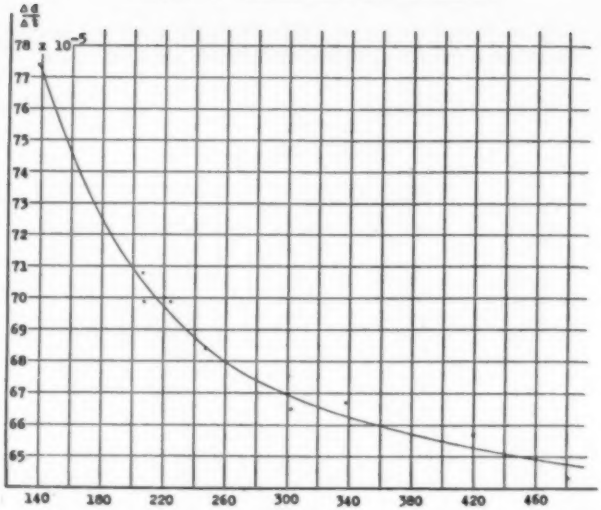

FIG. 2.

TEMPERATURE–DENSITY RELATIONSHIP PLOTTED AGAINST MOLECULAR WEIGHT.

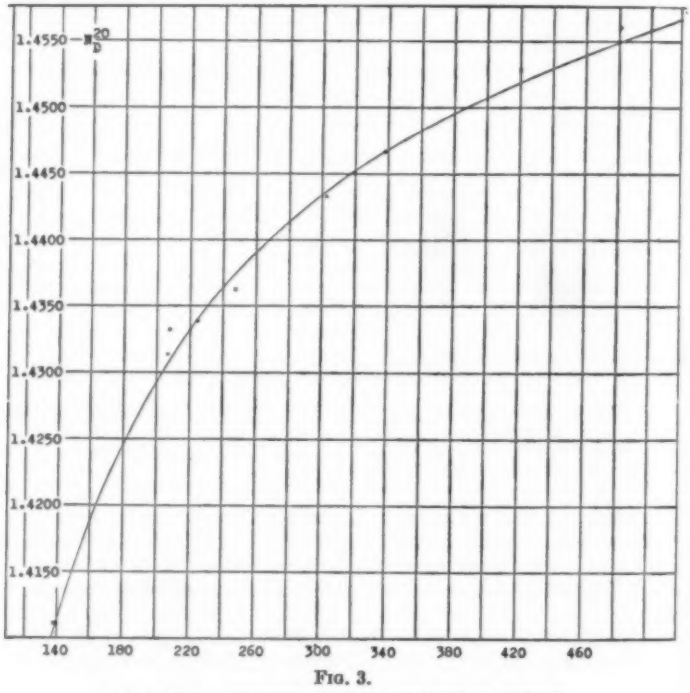

FIG. 3.

REFRACTION PLOTTED AGAINST MOLECULAR WEIGHT.

Certain deviations are observed by comparing the figures for the specific refraction with those calculated from the atomic refractions of Eisenlohr. A comparison with the average results shows that in practice higher values are obtained, the difference being in our case 0·0009. According to other

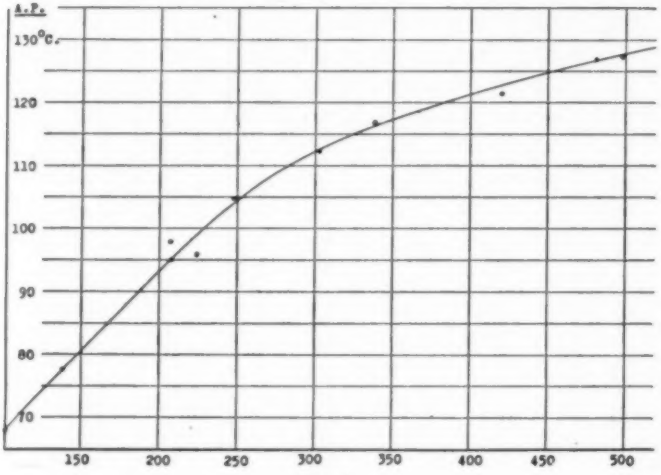

FIG. 4.

ANILINE POINT PLOTTED AGAINST MOLECULAR WEIGHT.

observations we consider the atomic refractions from Eisenlohr as being, in every case, partly responsible for this phenomenon. They seem to be somewhat too low.

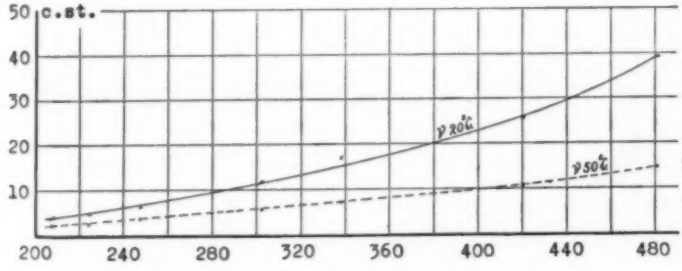

FIG. 5.

VISCOSITY IN CENTISTOKES (AT 20° AND 50° C.) PLOTTED AGAINST MOLECULAR WEIGHT.

The average temperature–refraction relationship was found to be 0·00038/°C. (max. 0·00040; min. 0·00034). No sharp relationship with regard to the molecular weight could, however, be found.

The Conradson value was also determined for the various samples. As

we were here dealing with saturated hydrocarbon mixtures, values varying from zero to traces were obtained.

Finally, with regard to viscosities, it was at first expected that the coefficient of direction m from the temperature–viscosity equation (Ubbelohde) could be brought into a certain relationship with the molecular

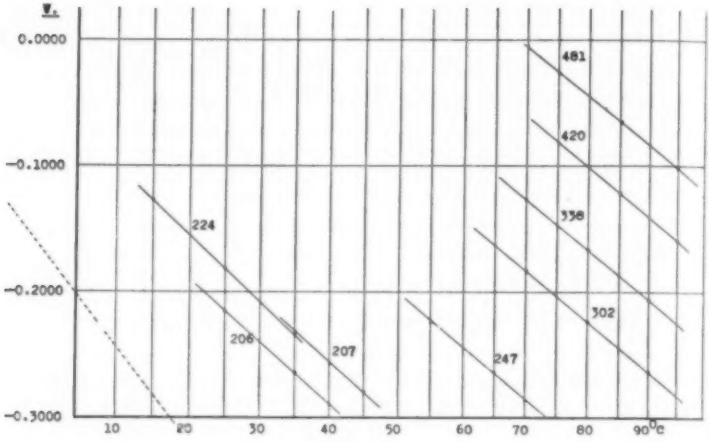

FIG. 6.

TEMPERATURE–VISCOSITY RELATIONSHIP ACCORDING TO UBBELOHDE.

weight of the paraffins investigated. This, however, was not the case, since m is too sensitive, even for variations well within the accuracy of the test. The following results were obtained for the paraffin with molecular weight 224; at 15° C. = 4·77 centistokes; at 25° C. = 3·74 centi-

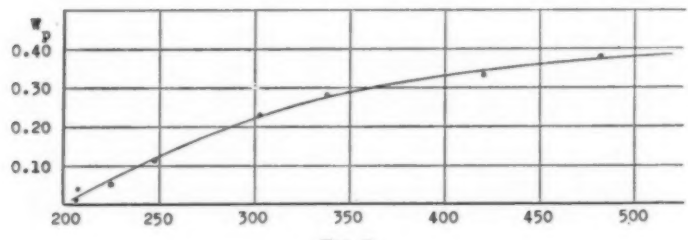

FIG. 7.

"VISCOSITY-POLE" PLOTTED AGAINST MOLECULAR WEIGHT.

stokes and at 35° C. = 3·04 centistokes. If m is calculated for the range 15–25° C., it is found to be 3·71, but for the range 25–35° C. 3·55. Therefore it is better to use the less-sensitive "viscosity-pole" (Fig. 7). It is apparent from Fig. 7 that W_p depends to a certain amount on the mole-

cular weight and tends to approach a constant end-value at higher molecular weight. As this is coupled with an increasing viscosity, it explains

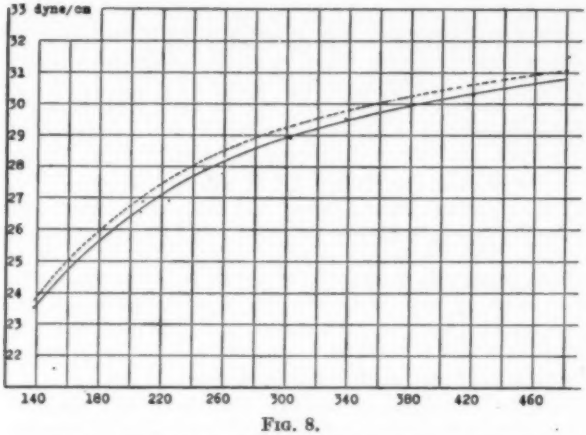

FIG. 8.

SURFACE TENSION PLOTTED AGAINST MOLECULAR WEIGHT.

The dotted line is that for the theoretical value, and is calculated from the specific parachor according to Mumford and Phillips and the average value for the density as given in graph 1.

Ubbelohde's remark that it is only permissible to reach conclusions regarding the origin of an oil from its "viscosity-pole," if the oil in question has a viscosity exceeding 20 centistokes at 50° C.

Laboratory for Oil- and Coal-Chemistry,
"Glückauf,"
Rotterdam.

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THE PRINCIPLES OF SOLVENT DEWAXING. PART IV.—THE PRECIPITATION OF WAX FROM SOLUTION IN OIL BY OIL-MISCIBLE LIQUIDS.*

By M. Ba Thi, B.Sc., A.I.C. (Student Member),
T. G. Hunter, Ph.D., B.Sc., A.R.T.C., A.I.C. (Member)
and A. W. Nash, M.Sc., M.I.Mech.E., M.I.Chem.E. (Member).

It has been previously shown [1, 2, 3] in the system oil-refined wax-solvent, using either single or mixed solvents, that equilibrium data may be satisfactorily represented by triangular diagrams. It is the aim of the present and future papers in this series to discuss the application of such diagrams to certain aspects of solvent dewaxing processes.

Perhaps one of the most interesting questions concerned with solvent dewaxing is that described in the present communication—namely, the possibility of obtaining a dewaxing solvent which acts as a wax precipitant.

In order to avoid ambiguity, the usual technical and rather misleading term dewaxing "solvent" will be referred to in the following discussion as dewaxing liquid. Consequently the words solvent, diluent or precipitant wherever they occur hereafter are to be read as possessing their usual exact physical significance. Considerable confusion undoubtedly exists in the literature on dewaxing by reason of the indiscriminate reference to dewaxing liquids as solvents, diluents or precipitants without regard to the exact physical behaviour of the liquids themselves.

It has been found that the addition of a liquid to a solution, with which it can form a homogeneous whole, can sometimes cause precipitation of a dissolved solute, provided that the solute is comparatively insoluble in the added liquid. This fact is utilized in the precipitation of salts from their solutions; thus the addition of alcohol to aqueous solutions of certain salts brings about their precipitation. In these cases the solute is less soluble in the mixture of the two liquids than it is in the original solvent.

The solubility curves for some systems of this type are plotted on the triangular graph of Fig. 1. It is obvious from the diagram that certain salts may be precipitated from their aqueous solution by the addition of alcohol.

This phenomenon suggests that the precipitation of wax from a solution in oil, by the addition of an oil-miscible liquid, may be possible in a similar manner. It is obvious that a liquid of this nature would be exceedingly valuable as a dewaxing liquid.

Some evidence is to be found in the literature for the existence of precipitating liquids for dewaxing. Maksorov [4] classifies liquids suitable for separating paraffin wax from oils into the following three classes :—

* Paper received July 30th, 1938.

(1) Those liquids the use of which results in no appreciable increase in the amount of solid phase formed when the quantity of the added liquid is increased.

(2) Those liquids the use of which results in the amount of solid phase increasing with increase in the amount of liquid added.

(3) Those liquids the use of which results in the amount of solid phase decreasing with increase in the amount of liquid added.

It would appear from the above that Class 1 liquids behave entirely as diluents. Class 2 liquids behave as precipitants; although most of

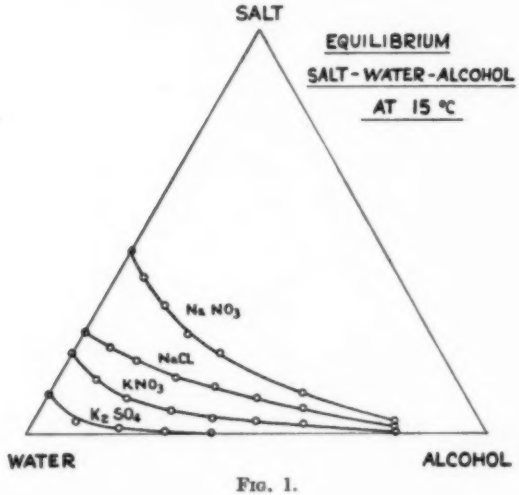

FIG. 1.

the examples quoted by Maksorov usually form two layers with oil, and hence do not come under the category of oil-miscible liquids discussed in the present paper. Class 3 type liquids are really solvents capable of dissolving any wax already present as a solid phase.

It should be pointed out here that a rigid classification of dewaxing liquids is not strictly possible. A particular liquid, for example, may behave either as a class 1, 2 or 3 type liquid, depending on the nature of the wax–oil mixture being treated and on the temperature conditions.

Further evidence for the existence of precipitating-type liquids is to be found in the literature. This evidence is of an indirect and rather inconclusive character. It consists of the fact that in dewaxing operations the pour points of the dewaxed oils sometimes are lower than the chilling temperatures. That is, a negative dewaxing differential is sometimes obtained. This phenomenon may be due to several causes :

(1) The dewaxing liquids used behave as liquids of the precipitating type.

(2) The liquids used behave as liquids of the diluent type.
(3) Pour-point depressants are present in the dewaxed oil.

In Fig. 2 an oil stock of composition P is to be dewaxed using a dewaxing liquid/stock ratio of PL/LS at a temperature of 79° F., the equilibrium curve for the system at this temperature being represented by AS, which is the type of curve obtained when the liquid used belongs to the precipitant type. From the diagram it can be seen that the composition of the dewaxed oil is given by N, which contains less wax than A, the composition of the wax-saturated, liquid-free oil at 79° F. The oil–wax

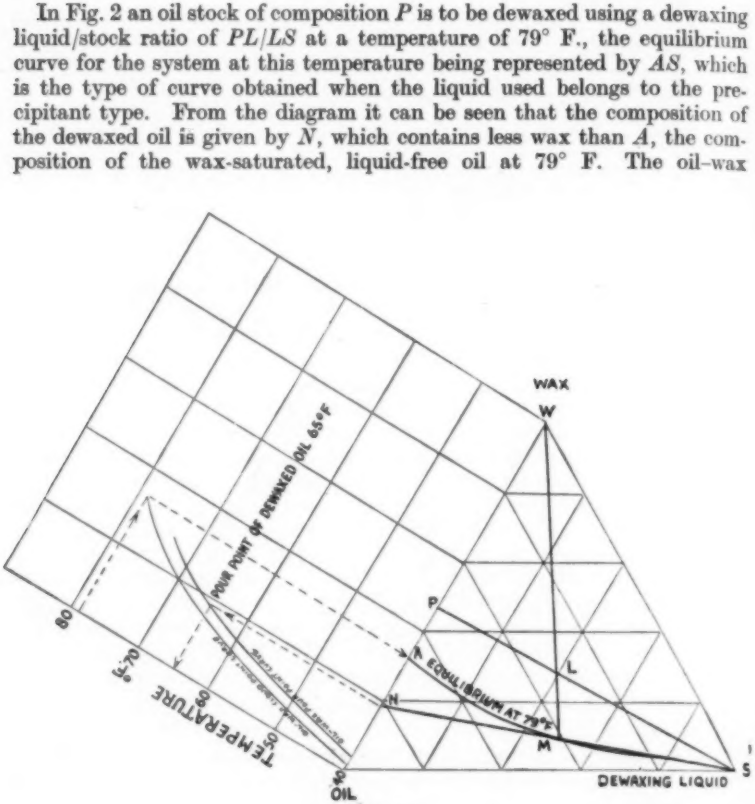

FIG. 2.

mixture which determines point A is that mixture which has a cloud point equal to the equilibrium or dewaxing temperature, and in the diagram is that mixture having a cloud point of 79° F. Since the dewaxed oil N has a lower wax content than A, the cloud point of the dewaxed oil N must be lower than the equilibrium or dewaxing temperature. The pour point of the dewaxed oil N, 65° F. for the example illustrated in Fig. 2, must also be lower than the dewaxing temperature—namely, 79° F. in this figure. Therefore any dewaxed oil which has a wax content equal to or lower than that represented by point A must have a pour point lower than the dewaxing temperature. In the case of a precipitating-type liquid, which possesses an equilibrium curve similar to AS, the point representing the composition of the dewaxed oil will always fall below point A. Hence

for precipitating liquids the pour point of the dewaxed oil is always below the dewaxing temperature.

The fact that pour points of dewaxed oil lower than the dewaxing temperature are sometimes recorded indicates that dewaxing liquids capable of precipitating wax from a solution in oil may possibly exist. This evidence is by no means conclusive, however, as a negative differential may be due to other causes.

In Fig. 3 the equilibrium curve AS is a typical curve for the purely diluent type of liquid, at a temperature of $T°$ F. It will be seen from this figure that, whatever the liquid/oil ratio, the composition of the dewaxed oil will always be represented by point A. That is, the pour point of the

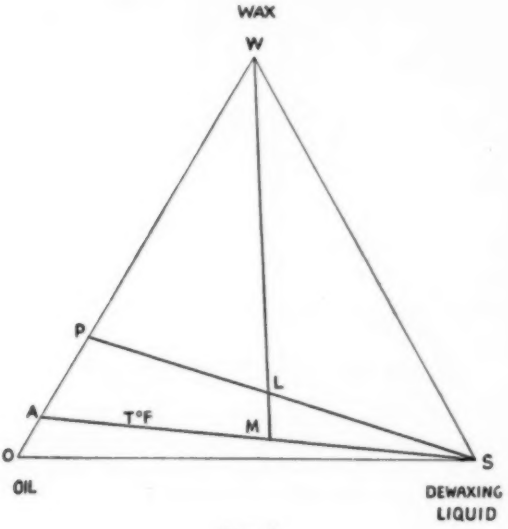

FIG. 3.

dewaxed oil will always be slightly lower than the dewaxing temperature.

It is obvious from the above considerations that when the pour point of a dewaxed oil is lower than the chilling temperature, the liquid employed may sometimes be acting as a wax precipitant. It will be clear also from the above that since this is not the only explanation of this phenomenon, that fact that in dewaxing operations a negative differential is sometimes obtained is by no means conclusive evidence for the existence of wax-precipitating liquids.

Examination of the dewaxing results available in the literature shows that with very few exceptions the pour points of the dewaxed oils are higher than the chilling temperatures. Different methods of dewaxing, different oil stocks, different dewaxing liquids, different temperatures, different liquid/oil ratios, have been used, but in the majority of cases the pour point of the dewaxed oil is higher than the chilling temperature.

In Table I various cases are given where the pour point of the dewaxed oil is lower than the chilling temperature.

TABLE I.

Stock.	Dewaxing Liquid Used.	Liquid/Oil Ratio, by vol.	Chilling Temp., ° F.	Pour Point of Dewaxed Oil, ° F.	Dewaxing Differential, ° F.	Reference.
Long residuum	Methylene chloride 80%, acetone 20%.	2 : 1	−13	−15	− 2	5
Wax distillate	Methylene chloride 50%, acetone 50%	4 : 1	−13	−25	−12	5
Mid-Continent distillate	Dichlorethane	3 : 1	+23	+21	− 2	6
,, ,,	,,	3 : 1	− 4	−10	− 6	6
,, ,,	,, + P	3 : 1	− 4	−24	−20	6
,, ,,	,,	1 : 1	− 4	−16	−12	6
,, ,,	,, + P	1 : 1	− 4	−25	−21	6
,, ,,	,,	5 : 1	− 4	−13	− 9	6
,, ,,	,, + P	3 : 1	− 4	−25	−21	6
Lobitos distillate	,,	4 : 1	+27	+ 9	−18	6
,, ,,	,,	4 : 1	+ 5	+ 2	− 3	6
,, ,,	,, + P	4 : 1	+14	− 7	−21	6
Alsacian distillate	,,	3 : 1	+14	+ 2	−12	6
,, ,,	,, + P	3 : 1	+14	+ 0	−14	6
,, ,,	,, + P	3 : 1	− 4	−11	− 7	6
Roumanian distillate	,, + P	4 : 1	+14	+ 3	−11	6
,, ,,	,,	4 : 1	− 4	− 6	− 2	6
,, ,,	,, + S	4 : 1	− 4	− 6	− 2	6
Iraq light distillate	Dichlorethane	2 : 1	+ 3	− 4	− 7	6
,, ,,	,, + P	2 : 1	+ 7	− 4	−11	6
,, ,,	,, + S	2 : 1	− 2	− 4	− 2	6
Iraq heavy distillate	,,	2 : 1	+ 2	− 4	− 6	6
Raw light coastal distillate	Benzol 50%, methyl ethyl ketone 50%	—	−40	−55	−15	7

P = Liquid added to precipitate asphalts, resins, etc.
S = Liquid added to dissolve asphalts, resins, etc.

In Table II are also given the results of dewaxing various stocks with an ethylene dichloride–benzene mixture,[9] using a two-stage process with a cake de-oiling wash in the second stage; here again the pour point of the dewaxed oil is lower than the chilling temperature.

TABLE II.

Stock.	Dewaxing Liquid Used.	Liquid/Oil Ratio for Dewaxing, by vol.	Liquid/Oil Ratio for Cake Washing, by vol.	Chilling Temp., ° F.	Pour Point of Dewaxed Oil, ° F.
Mid-Continent lubricating distillate	Methylene chloride + benzol	3	1·5	−9	−18
Mid-Continent vacuum cylinder stock	,, ,,	3	1·5	−5	− 6
Mid-Continent cylinder stock	,, ,,	3·25	1·5	+1	−10
East Texas dark residue	,, ,,	4	2·0	+3	− 8
Mid-Continent cylinder stock filtered	,, ,,	3	1·5	+1	− 2

It will be seen from these tables that a negative differential is obtained with a variety of stocks, temperatures and liquid/oil ratios. It will be observed also that the dewaxing liquids employed are ketones or chlorinated hydrocarbons, or mixtures of these either with or without benzol. Under

the conditions employed, these particular liquids may belong to either the purely diluent or precipitant class. The liquids mentioned in Tables I and II could undoubtedly behave as liquids of any one or all of these types, and adequately explain the phenomenon.

If a pour-point depressant were present in the original stock, this substance would tend to be adsorbed and removed by the solid wax phase and hence be absent from the dewaxed oil. If, however, the dewaxing liquid used had a high solvent capacity for the depressant, then the depressant would tend to be concentrated in the dewaxed oil. It is a pertinent fact that in the manufacture of Paraflow, chlorinated hydrocarbon solvents,[5] such as carbon tetrachloride,[6] are used to extract the active pour-point depressing

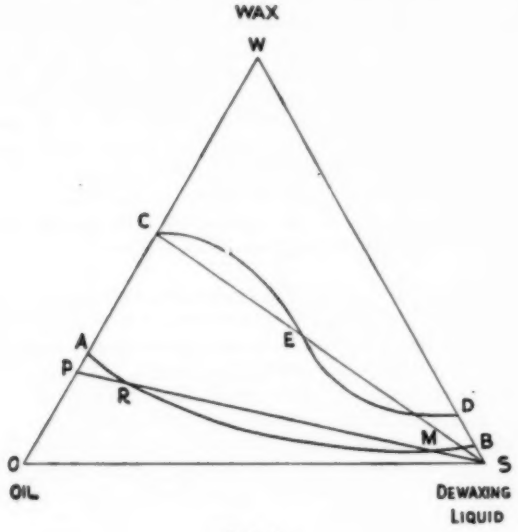

FIG. 4.

substances from the reaction mixture. The fact that the pour point of the dewaxed oil is lower than the chilling temperature when ketone and chlorinated hydrocarbon liquids are employed may well be due to the extraction by such liquids of active pour-point depressing substances from the solid wax and their resultant concentration in the dewaxed oil.

While the occurrence of a negative dewaxing differential may be due to any one of several causes, including the behaviour of the dewaxing liquid as a precipitating liquid, no evidence exists which enables any particular case to be singled out as due to precipitating action. Nevertheless the possible existence of wax-precipitating liquids cannot be overlooked, and, in consequence, it was felt that the question was worthy of investigation.

In Fig. 4 let *AB* represent the equilibrium at *T*° F., for a certain wax–oil–liquid system, the liquid behaving primarily as a wax precipitant.

If at a temperature $T°$ F. an unsaturated wax–oil mixture of composition P be titrated with the dewaxing liquid, the composition of the wax–oil mixture will travel along PS until it reaches R, when the wax will begin to be precipitated. The liquid/oil ratio at which precipitation begins will be equal to RP/RS. For the equilibrium type represented by curve AB, it is obvious that precipitation ceases altogether at point M, where the liquid/oil ratio equals PM/MS, and at liquid/oil ratios above this the dewaxing liquid is behaving as a solvent. If a saturated wax–oil mixture, say of composition represented by point A in the figure, be titrated with dewaxing liquid, solid wax will begin to be precipitated immediately. If, however, the equilibrium curve be similar to curve CD in the figure, precipitation will not begin, even when titrating a saturated solution such as that represented by point C, until point E is reached, where the liquid/oil ratio is equal to CE/ES. An easy method of detecting precipitating action by a dewaxing liquid is obviously the titration of a saturated wax-oil solution with such a liquid at a constant temperature equal to the saturation temperature. The use of a saturated wax–oil solution for this purpose requires accurate temperature control, as a slight fall in temperature may cause deposition of solid wax. It was found that a convenient way of obtaining a suitable saturated wax–oil solution is to take a wax–oil mixture and raise it to a temperature slightly above its cloud point or saturation temperature. On titrating at the saturation temperature with a liquid behaving as a precipitant, deposition of wax should then take place as shown above.

This titration method was therefore employed to examine a large variety of liquids in order to see if they would behave as wax precipitants. It was first discovered that wax could be precipitated from naphtha or benzol solution by several hydrocarbon miscible liquids. It appeared from this that wax was more readily precipitated from a solution in a hydrocarbon liquid of low molecular weight in which it was very soluble.

Therefore for this work a light lubricating oil was selected as the oil-solvent medium. It was hoped that by this means liquids behaving as wax precipitants would be detected more readily. The oil employed had the following characteristics :—

Sp. G. $\frac{60° \text{ F.}}{60° \text{ F.}}$	0·895/900
Closed flash point	390° F.
Open flash point	405° F.
Redwood viscosity 70° F.	400 secs.
„ „ 140° F.	72 „
„ „ 200° F.	42 „
Pour point	30° F.
Aniline point	191·7° F. (88·7° C.)

The wax employed was a refined Burma wax of 108° F. m. pt. A saturated wax–oil solution was titrated with different oil-soluble liquids at temperatures slightly above the cloud point or saturation temperature of the wax–oil mixture. The saturated wax–oil solution was first titrated at a temperature of 60° F. In case temperature was affecting precipitation, a wax–oil mixture which was saturated at the higher temperature

TABLE III.

Hydrocarbons.	Alcohols.	Ketones.	Amines.	Aldehydes.	Halogen Compounds.	Esters.	Miscellaneous.
1. Toluene	7. Ethyl alcohol*	15. Acetone*	19. Aniline*	21. Butyraldehyde	23. Ethylene chlorhydrin*	28. Ethyl formate*	46. Carbon disulphide
2. Turpentine	8. Methyl propyl alcohol	16. Acetophenone	20. Dimethyl-aniline	22. Heptaldehyde	24. *N*-Butyl iodide	29. Ethyl acetate	47. Acetic acid*
3. Dekalin	9. Dimethyl ethyl alcohol	17. cyclo Hexanone			25. Tetrachlor-ethane	30. Amyl acetate	48. *M*-Cresol
4. Cineole	10. *iso*Butyl alcohol	18. Methyl ethyl ketone			26. Amylene dichlorides	31. Cellosolve acetate*	49. Nitrobenzene*
5. Ethyl benzene	11. *N*-Butyl alcohol				27. Benzyl chloride	32. cyclo Hexyl acetate	50. Pyridine*
6. Amylene	12. *sec.*-Butyl alcohol					33. Octyl acetate (2-ethyl hexyl)	51. Propyl ether
	13. Benzyl alcohol*					34. Hornyl acetate	
	14. cyclo Hexanol					35. Methyl propionate	
						36. Ethyl propionate	
						37. *N*-Butyl propionate	
						38. Amyl propionate	
						39. Methyl levulerate	
						40. Ethyl levulerate	
						41. *N*-Butyl valerate	
						42. *iso*Butyl valerate	
						43. Amyl valerate	
						44. Ethyl laurate	
						45. Ethyl benzoate	

* Form two layers with the oil.

of 80° F. was used for titration with oil-soluble liquids at this temperature. As shown in Table III, over fifty organic liquids, mostly oil-soluble, and comprising hydrocarbons, alcohols, ketones, amines, aldehydes, halogen compounds and esters, were tried at the two temperatures of 60° and 80° F. In some cases the solvent formed two layers with the oil, but in no case was any precipitation of wax detected.

However, in the case of a saturated solution of refined Burma wax in naphtha or benzol, at a temperature of 60° F., both acetone and amyl alcohol were found to produce flocculent precipitation of wax, whilst ethyl acetate and methyl ethyl ketone when added to these solutions first precipitated and then redissolved wax.

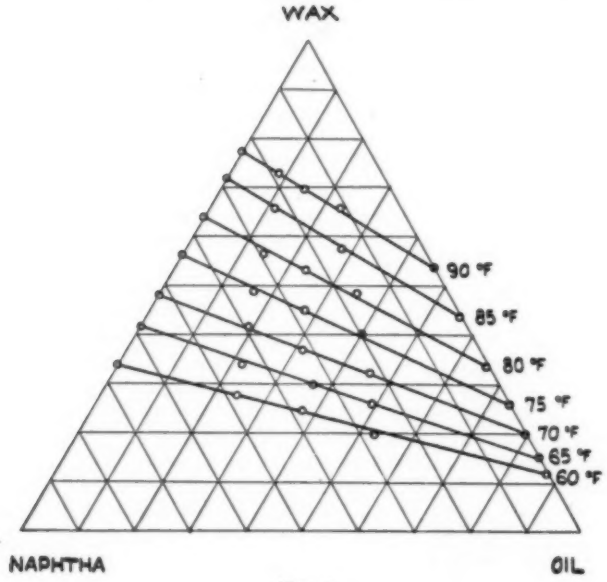

FIG. 5.

It is apparent from the above data that wax may be precipitated from a hydrocarbon solvent by the addition of another suitable hydrocarbon-miscible liquid. But precipitation appears to be governed by certain special conditions. For example, no precipitation was obtained from a saturated solution of wax at a temperature of 60° F. in light lubricating oil by the addition of acetone, ethyl acetate or methyl ethyl ketone. However, precipitation was obtained from a saturated solution of the same wax in naphtha or benzol at a similar temperature, by the addition of these liquids.

With the object of explaining these data, further experiments were carried out to investigate the conditions under which a liquid can precipitate wax from solution in a solvent.

Three non-precipitating-type systems of Burma wax, m. pt. 108° F.,

with Anglo-Iranian second cooled blue oil using naphtha, ethyl acetate and methyl ethyl ketone as the added liquids, respectively, were selected. Complete equilibria for these three systems were determined over the temperature range 60–90° F. The results for these systems are shown in graphical form by the equilibrium diagrams of Figs. 5, 6 and 7. Next four precipitating-type systems were selected consisting of wax with naphtha, using methyl ethyl ketone, ethyl acetate and amyl alcohol as the added liquids, and of wax with benzol using acetone as the added liquid. Complete equilibria for these systems were determined over the same temperature range, the results being shown in Figs. 8, 9, 10 and 11. It

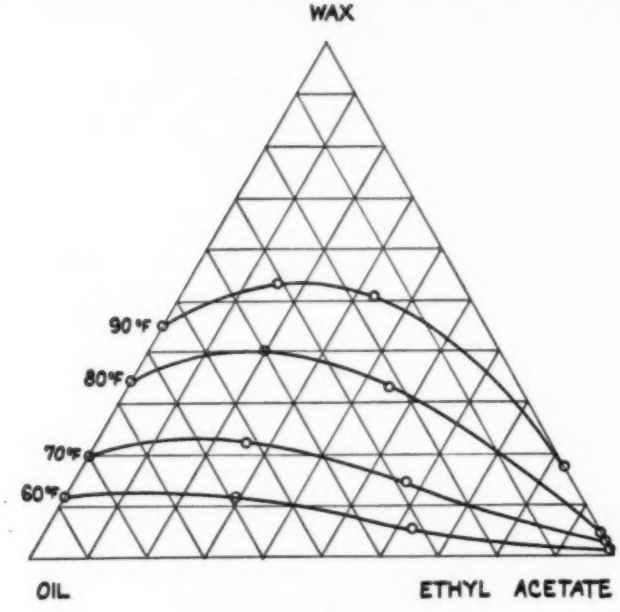

FIG. 6.

was hoped that by a comparison of the non-precipitating-type systems with the precipitating-type systems some of the conditions for precipitation could be evaluated.

Referring to Figs. 5, 6 and 7, it will be noticed that none of the equilibrium curves has the same form as the salt-water–alcohol curves of Fig. 1—that is, the liquids naphtha (110–120° C.), methyl ethyl ketone and ethyl acetate do not behave as wax precipitants for a Burma wax–Anglo-Iranian second cooled blue-oil mixture over the temperature range 60–90° F.

In the case of the precipitating-type systems, however, illustrated in Figs. 8, 9, 10 and 11, at certain temperatures some of the equilibrium curves have the same form as the salt-water–alcohol curves in Fig. 1.

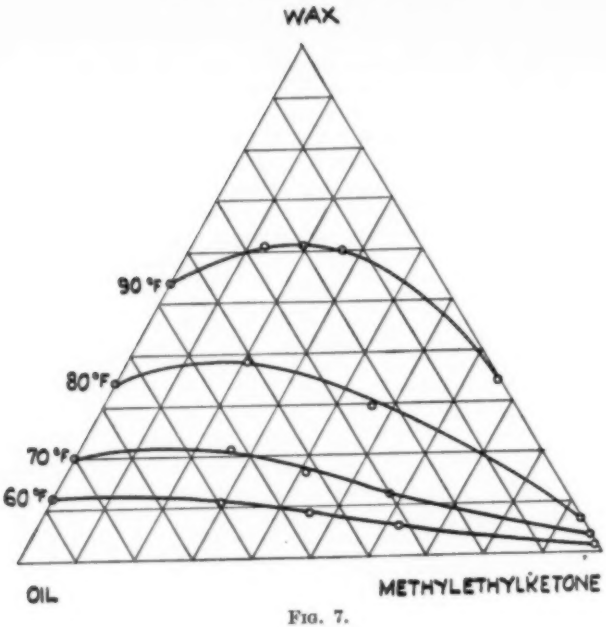
WAX
90 °F
80°F
70 °F
60 °F
OIL
METHYLETHYLKETONE

FIG. 7.

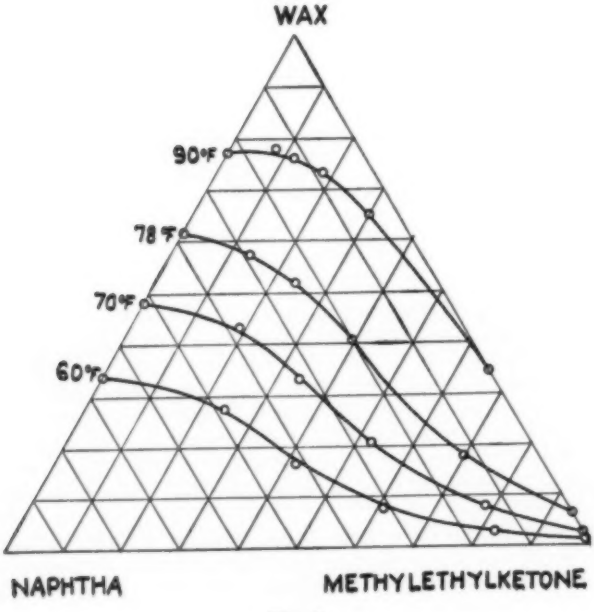
WAX
90°F
78 °F
70°F
60°F
NAPHTHA
METHYLETHYLKETONE

FIG. 8.

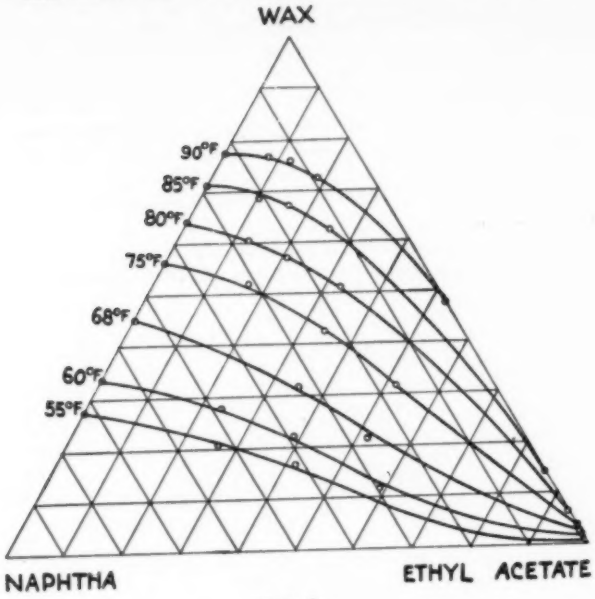
WAX
90°F
85°F
80°F
75°F
68°F
60°F
55°F
NAPHTHA
ETHYL ACETATE

FIG. 9.

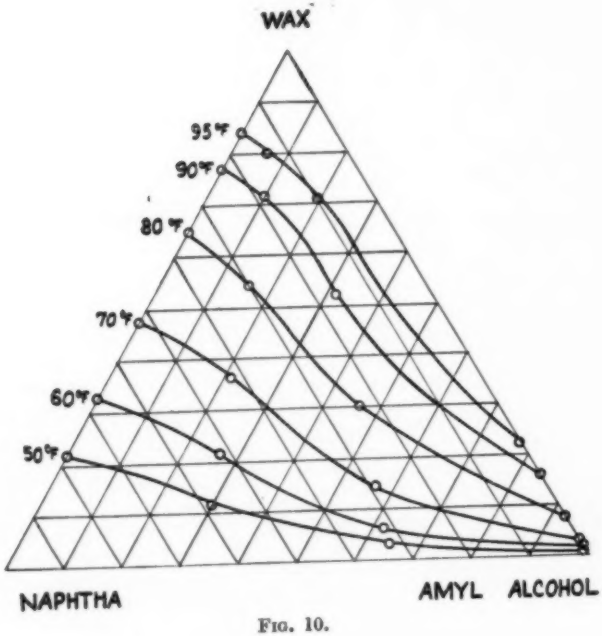
WAX
95°F
90°F
80°F
70°F
60°F
50°F
NAPHTHA
AMYL ALCOHOL

FIG. 10.

The liquids, methyl ethyl ketone, ethyl acetate, amyl alcohol and acetone, possessing these curves are behaving as wax precipitants at these temperatures.

From an inspection of the data obtained, it appeared that the difference in solubility of the wax in the hydrocarbon and dewaxing liquids of any such system controlled precipitation to some extent. This difference in solubility, $S_1 - S_2$, of the wax in the hydrocarbon and dewaxing liquids over the appropriate temperature range has been plotted against temperature in ° F. in Fig. 12.

It will be seen from this figure that the wax-solubility differences $S_1 - S_2$ for the precipitating-type systems are very much in excess of the

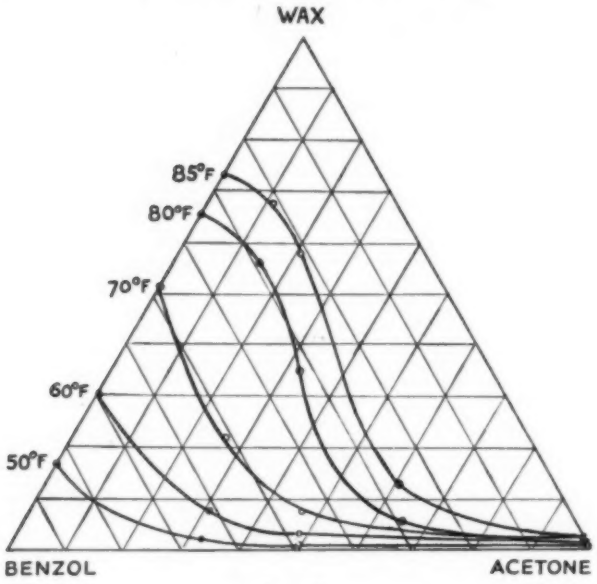

FIG. 11.

solubility differences for the non-precipitating-type systems. All the $S_1 - S_2$ temperature curves pass through a maximum. The difference between the precipitating- and non-precipitating-type systems is very well defined by these curves. It would appear that the solubility difference $S_1 - S_2$ is a factor which would govern to some extent the precipitation of wax from a solution by the addition of a dewaxing liquid.

It is obvious also from this figure that although the solubility difference $S_1 - S_2$ is the same for the same system at two different temperatures, precipitation occurs only at the lower temperature. The true factor which would therefore appear to govern precipitation is not solubility difference alone, but solubility difference combined with certain temperature conditions.

In Figs. 6, 7, 8, 9, 10 and 11 a definite flattening of the solubility curves is noticeable with decreasing temperature. At the low temperatures normally prevailing in dewaxing operations any precipitating action would probably tend to be decreased. It would have been desirable to extend the present investigation into this low temperature region, but at the moment this has not been possible, although it is hoped to do so at some future

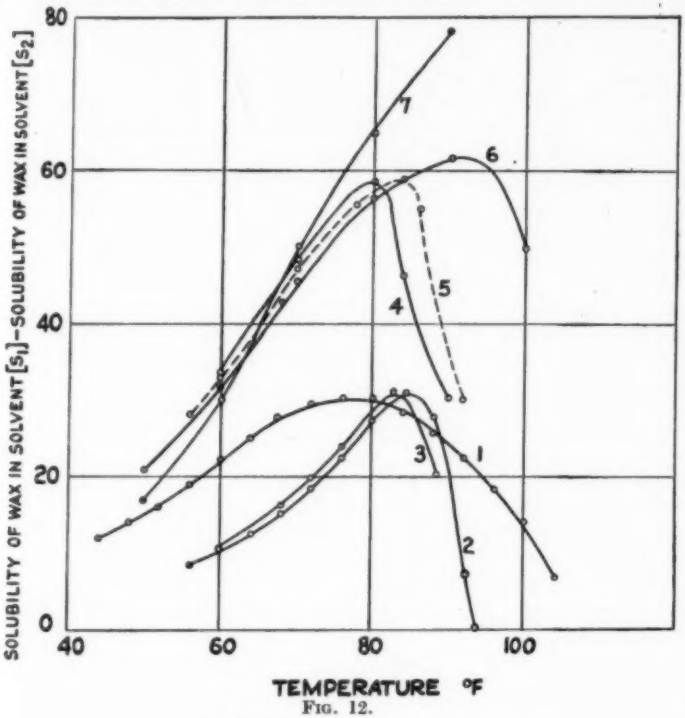

FIG. 12.

1. Naphtha–Oil.
2. Oil–Methyl Ethyl Ketone.
3. Oil–Ethyl Acetate.
4. Naphtha–Ethyl Acetate.
5. Naphtha–Methyl Ethyl Ketone.
6. Naphtha–Amyl Alcohol.
7. Benzol–Acetone.

date. The possibility of the existence of dewaxing liquid capable of precipitating wax from its saturated solution in lubricating oil at normal dewaxing temperatures has therefore not yet been decided.

From the data obtained the possibility of the existence of a single liquid completely miscible with lubricating oil, and capable of precipitating wax from its saturated solution in such lubricating oil at temperatures above 50–60° F., appears to be remote, since the solubility of wax in lubricating oil even at temperatures higher than 50–60° F. is comparatively low.

Consequently even with a liquid in which the solubility of the wax was infinitesimal, the solubility difference, $S_1 - S_2$, would be low, and not within the solubility range required for precipitation.

Conclusions.

Summing up, the factors governing precipitation so far ascertained would appear to be :—

(1) The difference between the solubility of the wax in the hydrocarbon solvent and the added liquid must be above a certain minimum.
(2) The temperature at which precipitation is to take place must be below a certain maximum for a particular solubility difference.

These two factors are probably not the only governing conditions. Other variables as yet unaccounted for may have to be taken into consideration.

The possibility of wax precipitation by the use of dewaxing liquids which are mixtures of two or more substances has not been investigated, and the above remarks apply only to single liquids completely miscible with the oil.

It is emphasized here that the suitability of a liquid for dewaxing operations is dependent primarily on the solubility of wax in the oil in conjunction with the solubility of wax in such dewaxing liquid. These two factors should always be considered together. In most of the literature on dewaxing liquids the solubility of wax in the dewaxing liquid is taken as the only criterion of suitability. Occasionally consideration is given to the solubility of wax in mixtures of oil and dewaxing liquid; the wax solubility in the oil is never considered. These latter data should be taken in conjunction with the wax-liquid and wax-oil-liquid solubility data in determining the behaviour of a dewaxing liquid.

The occurrence of a negative dewaxing differential is largely a function of the behaviour of the dewaxing liquid. With stocks free from pour-point depressants a negative differential can be obtained if the dewaxing liquid is of the precipitant or diluent type. With stocks containing a pour-point depressant the occurrence of a negative differential caused by the behaviour of the dewaxing liquid may be enhanced by the maintenance of the depressant in the dewaxed oil by the solvent power of the dewaxing liquid. Depressant-containing stocks treated with solvent-type liquids may also show a negative differential due entirely to the concentration of depressant in the dewaxed oil through extraction by the dewaxing liquid.

Department of Oil Engineering and Refining,
The University of Birmingham.

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SPECIFIC REFRACTIVITY AND CARCINOGENICITY OF MINERAL LUBRICATING OILS.*

By Lt.-Col. S. J. M. Auld, O.B.E., M.C., D.Sc.

The 1934 report of the Manchester Committee on Cancer proposed a standard for mineral oils to enable the textile industry to choose oils which should be substantially free from those properties or constituents considered to contribute to the occupational disease of mule-spinners' cancer.

The suggested criterion is founded on an alleged relationship between carcinogenicity and the refractive index and specific gravity of the lubricating oil, and reads as follows :—

> "Mule-spindle mineral lubricating oils should have a specific refractivity below 0·5539 when the specific gravity is above 0·895, or a specific refractivity below 0·5569 when the specific gravity is below 0·895. By specific gravity is meant the specific gravity at 60° F. in relation to water at 60° F. vacuo/vacuo. By specific refractivity is meant $\frac{n-1}{d}$, where n is the refractive index for d line sodium light, and where d is density in grammes per millilitre at 20° C."

The density of the lubricating oil is an important factor in the specification. The specific gravity is directly proportional to the density, and a specific gravity of 0·895 is chosen as the dividing line below which and above which a different specific refractivity limit is required. Furthermore, the density of the oil is the divisor in the formula for determining the specific refractivity.

In view of the importance of the subject, it is natural that the validity of the Manchester Committee's conclusions should be closely examined.

The following data appear to throw doubt upon the acceptability of the method :

Fig. I.—*Specific Gravity Relationships of Mixed Oils.*

This chart shows the straight-line relationship between the specific gravity and the volume percentages of three series of mixtures of paraffinic oils obtained from Oklahoma City crude oil and naphthenic oils from Gulf Coast crude oil.

Figs. II, III and IV.—*Specific Refractivity Relationships of Mixed Oils.*

These charts indicate the relationships, for the same series of oils, of mixture percentages and specific refractivities. There is also shown,

* Paper received September 12th, 1938.

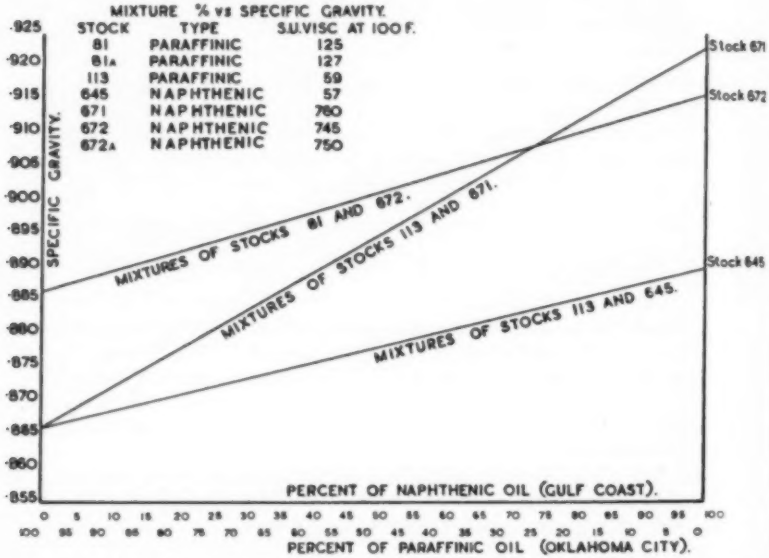
where applicable, the vertical line of 0·895 specific gravity corresponding to the mixture percentage; this is derived from Fig. I.

FIG. V.—*Viscosity and Specific Refractivity.*

This chart shows the relationship between the viscosity and the specific refractivity of pure oils of naphthenic and paraffinic types, together with an indication of the nature of refinement to which the oils have been subjected.

From reference to Figs. II, III and IV, it will be seen that certain areas of the charts, designated *A* and *B* respectively, represent two sets of con-

~FIG. I.~



ditions, each with an infinite variety of combinations, that would be held indicative of oil unsatisfactory for mule-spindle lubrication. *A* includes all oils having a specific gravity less than 0·895 and a specific refractivity greater than 0·5569. *B* includes all oils having a specific gravity greater than 0·895 and a specific refractivity greater than 0·5539.

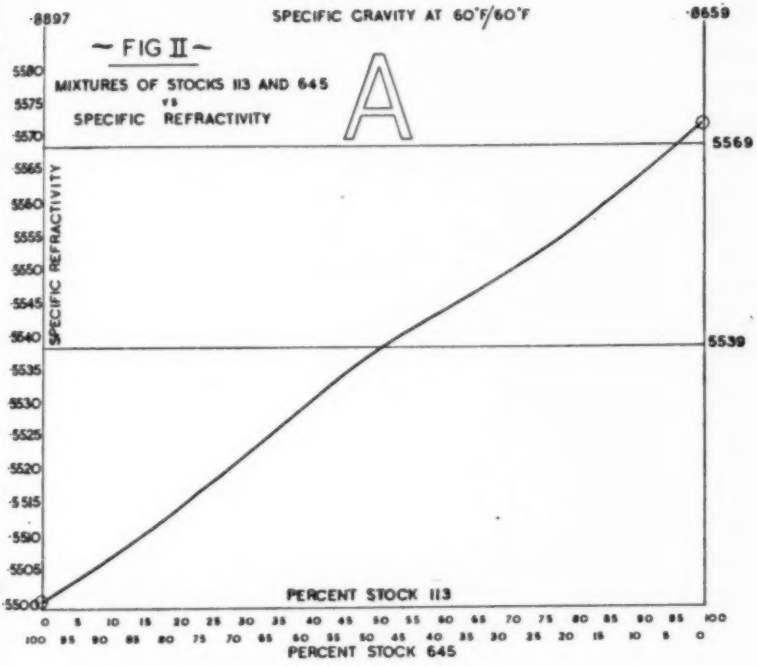
Fig. II shows that mixtures containing more than 97 per cent. of Stock 113 and less than 3 per cent. of Stock 645 would not meet the Manchester Committee specification. All other mixtures—that is, any containing greater than 3 per cent. of Stock 645—would be regarded as satisfactory.

From Fig. III it will be seen that mixtures containing from 33·0 to 49·0 per cent. of Stock 113 (with the complementary percentages of Stock 671) would not meet the Manchester Committee specification, as the mixtures within these limits lie in area *B*. Conversely, mixtures containing

any other percentages than those defined in the foregoing would be regarded as satisfactory.

Similarly, from Fig. IV it is clear that mixtures containing from 45 to 71 per cent. of Stock 81 and from 29 to 71 per cent. of Stock 81A would not meet the specification, since all mixtures within these limits fall in area *B*. Mixtures containing any other percentages not included within these limits would be regarded as non-carcinogenous.

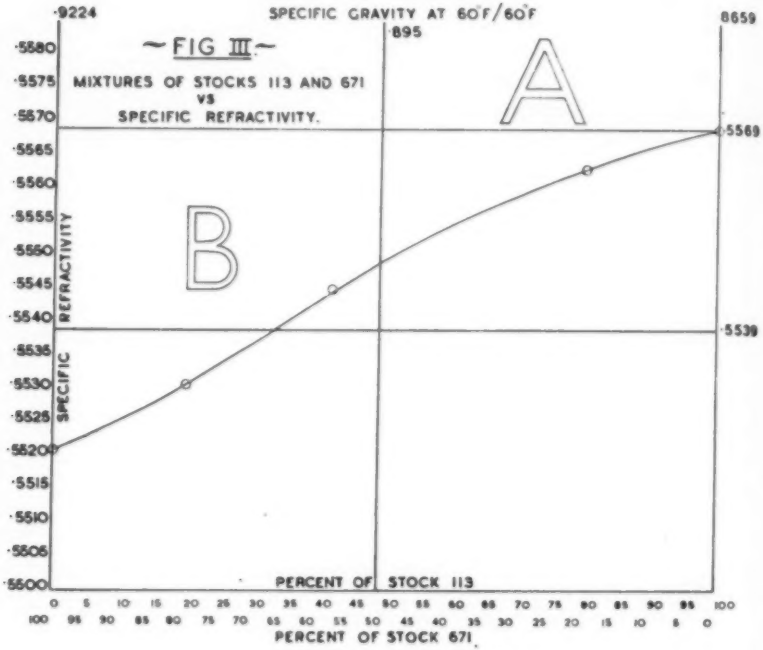
Three different types of relationship appear thus to have been established. In each the naphthenic oil (Stocks 645, 671 and 672) alone meets



the specification. On the other hand, the paraffinic oil in the case of Stock 113 does not, and in the case of Stock 81 does, meet the specification.

Since none of the mixtures shown in Fig. II attains a specific gravity of 0·895, all having a specific refractivity of less than 0·5569 are supposed to be satisfactory, and it only takes 3 per cent. or more of the naphthenic oil to establish this value. When, however, a somewhat more viscous naphthenic oil is used with the same paraffinic oil, the limit of 0·895 in specific gravity is reached before the specific refractivity has been reduced below 0·5539 (Fig. III). The same applies to the mixtures plotted in Fig. IV, except that in this case the more viscous paraffinic oil, Stock 81, would be regarded as being satisfactory alone.

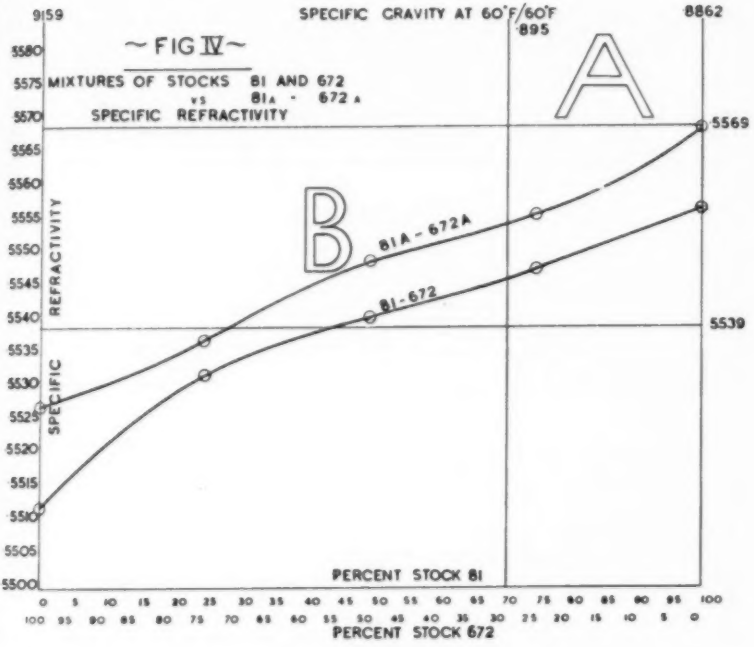
It is difficult to understand how two oils such as those illustrated by Fig. IV—*i.e.*, a paraffinic oil and a naphthenic oil—both of which meet the limit specific refractivity, should have cancer-forming propensities when admixed in percentages between the range of 45 per cent. and 71 per cent. and 29 per cent. and 71 per cent. of paraffinic oil, and not in mixtures of less or greater amount. It is likewise difficult to see how the addition of only 2 or 3 per cent. of naphthenic oil has such a nullifying effect on the cancer-forming ingredients of the paraffinic oil shown. It seems logical to conclude that the specification is not sound.



Of further interest are the data shown in Fig. V. To the left of the vertical line indicating a specific refractivity of 0·5539 are a number of naphthenic oils. In Oils *A*, *C* and *D* the specific refractivity increases slightly with increase in viscosity, although the difference is small and does not warrant conclusions being drawn. On the other hand, the oils K_2, L_2 and N_2, all of paraffinic origin from Oklahoma City crude oil, show a decrease in specific refractivity with increase in viscosity. Amongst the Coastal Oils Series A–A_1–A_2–A_3–A_4, each of which is successively more highly refined than the one preceding, the specific refractivity shows a marked decrease. This is also the case in Series D–D_1–D_2–D_3. On the other hand, amongst the paraffinic oils, the Series K_1–K_2–K_3 shows an

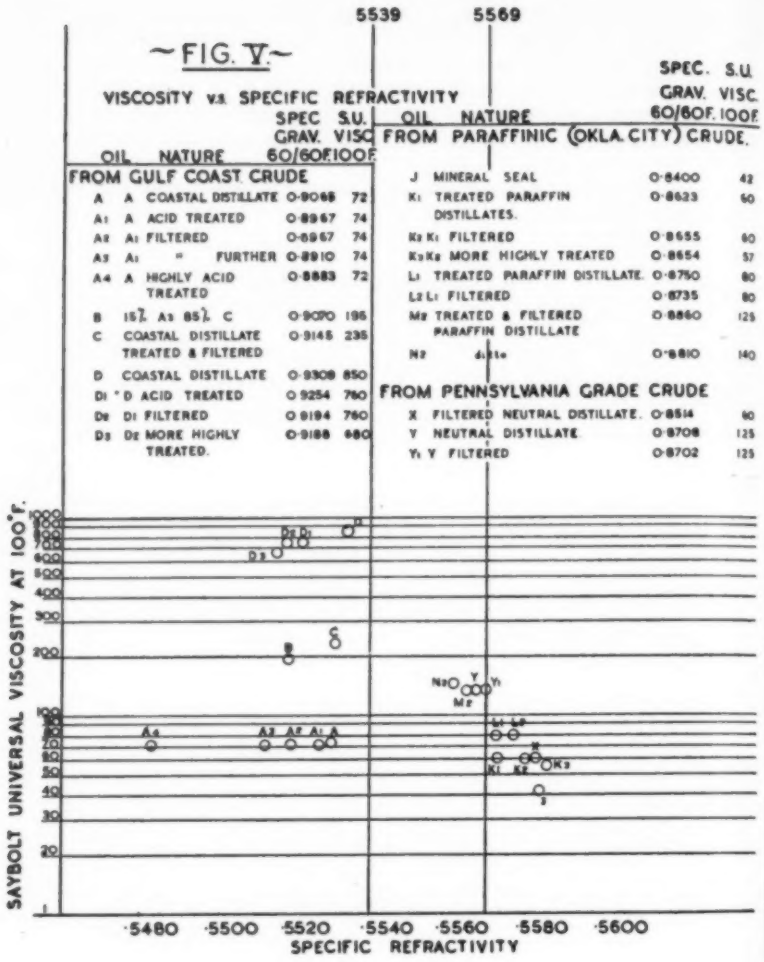
increase of specific refractivity with an increase in the extent of refinement. This is further confirmed by the Series L_1–L_2– and to a minor extent by the Pennsylvania Series Y–Y_1–. It will be observed that the trend here is the reverse of that exhibited by the naphthenic type of oil. If refining is to be regarded as a removal of ingredients potentially carcinogenic, the question arises, why does it not work in the same way with both types of oils by the same method of refining?

It would appear that there are serious inconsistencies in the Manchester Committee specification.



Since the issue of the specification the Manchester Committee in its 1935 report refers at length to a suggested test for the carcinogenicity (now extended to include dermaticity) of oils whereby the oil is evaluated by the action upon it of living animals. The oil concerned is injected into a mouse. After a suitable time the oil is removed and any modification of its physical properties noted. There is stated to be "a definite correlation between the refractive index fall and carcinogenic potency, viscosity and refractivity."

In view of the suggested questionable value of refractive index measurements as a means of determining carcinogenic potency, the proposed method *in vivo* must also fall under suspicion.



The results may be summarized as follows :

1. Two oils from different sources, both of them meeting the Manchester Committee specification when used alone, may be mixed in some proportions and fail to meet the specification, whereas in other proportions they comply.

2. Two oils of different types, of which the naphthenic oil meets and the paraffinic oil does not meet the specification, may when mixed in some proportions comply with the specification, whereas in other proportions they will not.

3. Naphthenic oils increase in specific refractivity with increase in viscosity and increase in specific gravity. Paraffinic oils decrease in specific refractivity with increase in viscosity and increase in specific gravity.

4. Naphthenic type oils decrease in specific refractivity with increase in the extent of refinement. Paraffinic oils increase in specific refractivity with increase in the extent of refinement. If refining removes the impurities causing cancer, the specific refractivity for refined lubricating oils is not a good measure of carcinogenicity.

5. Similar results are likely to be obtainable with other oils of different origin.

6. The foregoing conclusions must apply equally to tests with oils on living animals involving measurements of change of refractive index.

The author wishes to express his indebtedness to his colleagues of the Socony-Vacuum Oil Company, Inc., and the Vacuum Oil Company, Ltd., particularly Mr. R. B. Ogden, in connection with the preparation of this paper.

THE APPLICATION OF PHYSICO-CHEMICAL PRINCIPLES TO THE INVESTIGATION OF THE PROPERTIES OF ROCKS.

PART III.

POROSITY—COMPARISON OF METHODS AND CONCLUSIONS.

By A. H. NISSAN, B.Sc. (Student), C. E. WOOD, M.Sc., A.I.C. (Member), L. V. W. CLARK, M.Sc., M.I.Mech.E. (Member) and A. W. NASH, M.Sc., M.I.Mech.E. (Member).

SYNOPSIS.

In a previous paper the authors described two methods for available porosity determinations. In this concluding paper the two methods are compared with each other. The accuracy of each step is initially determined; then the overall accuracy of each method is calculated and demonstrated experimentally. Unidirectional errors of constant magnitude in either of the two methods will not be apparent on repeating the determination on any particular sample. Such errors will be evident, however, when results obtained by the two methods on the same sample are compared.

General conclusions point to the fact that the optimum value for bulk volume from the point of view of accuracy in porosity measurement and of ease in manipulation is 40 c.cs.

THE development of porosity measurement technique and apparatus was discussed in Part II * of this series. Although it was shown that total porosity could be measured to within an accuracy of $\pm$ 0·25 per cent. because of the fact that such measurement resulted in the destruction of the major portion of the sample, it was decided to confine the investigation to available porosity. The available porosity of a rock can be determined to within an accuracy of $\pm$ 0·25 per cent., greater accuracies being possible with a variation in bulk volume. The value of the available porosity was reported to the second decimal place in the previous paper, but such accuracy is unnecessary for practical purposes, and herein all values for porosities will be reported to the first decimal place.

Typical and detailed measurement readings and results in the several operations involved in porosity measurement are given to complete the record of this section of the research.

BULK VOLUME.

The pyknometer shown in Fig. 1 has already been described and the operation explained in Part II. There is one further observation of

* A. H. Nissan, C. E. Wood, L. V. W. Clark and A. W. Nash, *J.I.P.T.*, 1938, **24**, 370.

importance to be made. It was stated that to prevent the sample from touching the top of the pyknometer, and thus entrapping air between sample and glass, resulting in errors of indefinite magnitude, a piece of stout

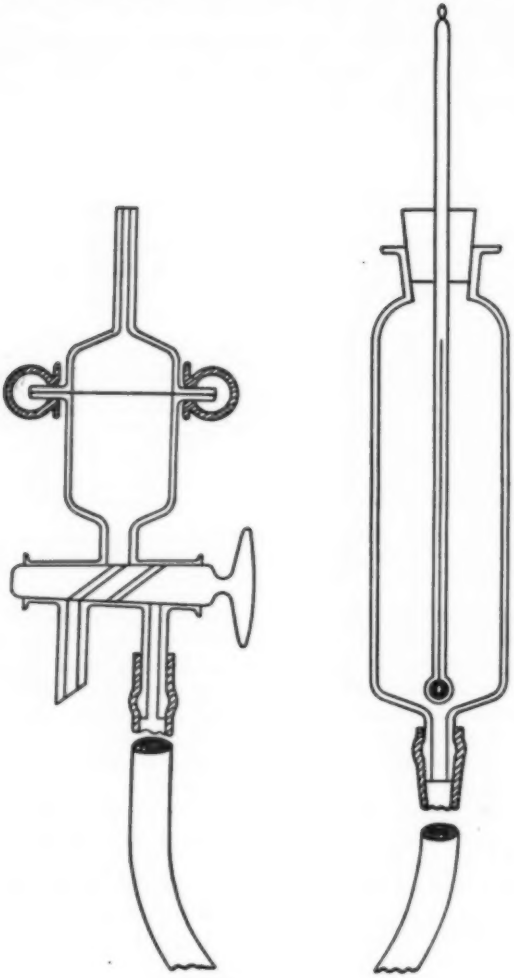


FIG. 1.

wire was thrust down the capillary tube, pushing the sample down and enabling the mercury to envelope it completely. This procedure was accurate, but it introduced a minor complication. The wire caused a cavity to be formed in the sample, and thus the sample became slightly

smaller in volume on successive measurements. The porosity was not affected by this cavity, but successive readings of volumes did not agree to the accuracy required. Table I illustrates this statement.

TABLE I.

	Bulk Volume, c.cs.	Available Volume, c.cs.	Volume of Voids, c.cs.	Available Porosity, per cent.	Deviation of Porosity from Mean Value, %.
1	21·95	16·98	4·97	22·6	+0·1
2	21·94	16·97	4·97	22·7	+0·2
3	21·92	16·98	4·94	22·5	—
4	21·90	17·02	4·88	22·3	−0·2
5	21·89	16·99	4·90	22·4	−0·1

This discrepancy was avoided by subjecting the air bubble adhering to the top of the pyknometer to pressure until it was too small to be discerned. After filling the pyknometer containing the sample with mercury, the top of the capillary was closed by the finger, and the reservoir raised, thus subjecting the small air bubbles to a head of mercury. Table II illustrates

TABLE II.

	Weight of Flask, gms.	Weight of Flask plus Mercury, gms.	Temperature of Mercury, ° C.	Specific Volume of Mercury, c.c./gms.	Bulk Volume of Sample (64·35–Vol. Hg.), c.cs.
	Sandstone				
1	56·224	669·807	16·4	0·073775	19·08
	56·183	669·629	18·0	0·073796	19·08
	56·369	670·420	14·9	0·073755	19·06
	56·182	670·127	16·9	0·073775	19·06
	56·235	670·011	19·2	0·073813	19·05
	Limestone				
2	56·236	631·552	19·8	0·073821	21·88
	56·244	631·608	19·1	0·073811	21·88
	56·168	631·318	21·2	0·073837	21·88
	56·275	631·379	17·5	0·073790	21·91

typical readings made on one sandstone and one limestone sample which were subjected to porosity measurement by the liquid-absorption method after each bulk-volume determination.

To eliminate the effects of " the personal equation," measurements by different workers were taken throughout these experiments, and in Table III the results obtained in the two series are tabulated.

It will be noted that for each worker the error is of the order of $\pm$ 0·03 c.c., or approximately $\pm$ 0·15 per cent. on the mean bulk volume. Taking the mean value obtained by each worker for the sample, the difference between the two means does not exceed 0·02 c.c., or approximately 0·1 per cent. on the bulk volume. The value of these errors appears to be a constant independent of the volume of the sample. Hence the percentage error is proportionally reduced by enlarging the bulk volume.

TABLE III.

Sample.	Bulk Volumes, c.cs.					Average.
	1.	2.	3.	4.	5.	
Sandstone						
A	18·17	18·18	18·15	18·14	18·13	18·15
	18·13	18·13	18·13	18·12	18·12	18·13
B	15·77	15·75	15·76	15·75	15·75	15·76
	15·76	15·76	15·76	15·76	15·75	15·76
C	16·08	16·08	16·07	16·07	16·07	16·07
	16·07	16·07	16·07	16·06	16·07	16·07
D	16·54	16·52	16·53	16·51	16·52	16·52
	16·52	16·53	16·52	16·54	16·51	16·52
Limestone						
A	21·70	21·70	21·71	21·70	21·71	21·70
	21·73	21·73	21·71	21·71	21·71	21·72
B	21·62	21·62	21·63	21·65	21·62	21·63
	21·69	21·62	21·64	21·63	21·65	21·65
C	21·89	21·85	21·86	21·84	21·85	21·86
	21·86	21·86	21·86	21·86	21·86	21·86
D	21·90	21·91	21·90	21·89	21·90	21·90
	21·92	21·92	21·90	21·91	21·90	21·91

APPARENT VOLUME.

1. *Liquid Absorption.*

The beaker fitted with a wire handle and suspended by a fine wire was used to determine the apparent volume of the samples in the manner described previously (Part II). Table IV illustrates the type of volume

TABLE IV.

Sample.	Apparent Volume, c.cs.					Average Apparent Volume, c.cs.	Maximum Deviation from Average Apparent Vol., c.cs.
	1.	2.	3.	4.	5.		
Sandstone							
I	13·56	13·58	13·58	13·58	13·57	13·57	±0·01
II	14·31	14·31	14·32	14·30	14·25	14·30	−0·05
III	11·74	11·76	11·75	11·74	11·76	11·75	±0·01
IV	12·03	12·02	12·00	12·04	12·03	12·02	±0·02
V	12·37	12·40	12·39	12·37	12·38	12·38	+0·02
Limestone							
I	17·49	17·43	17·48	17·46	17·43	17·46	±0·03
II	16·94	16·96	16·95	16·98	17·03	16·98	+0·05
III	16·42	16·37	16·39	16·36	16·38	16·38	+0·04
IV	16·83	16·85	16·87	16·86	16·88	16·86	−0·03
V	17·07	17·10	17·06	17·07	17·03	17·07	−0·04

measurements obtained by this method as performed on sandstone and limestone samples. It will be observed that the maximum deviation of any single determination for apparent volume by liquid absorption from the mean value of five determinations does not exceed 0·05 c.c. Since the bulk-volume measurements may be ± 0·03 c.c. from the mean value, it would appear that the apparent volume of the voids as determined by this process may be ± 0·08 c.c. from a mean of, say, five determinations.

Table V gives such determinations, and shows that the maximum deviation on fifty determinations does not exceed ± 0·05 c.c.—*i.e.*, the errors introduced in bulk and apparent volume measurements tend to annul each other to a certain extent. For a bulk volume of 20 c.cs. it will be seen that the available porosity value will be ± 0·15 per cent. from the mean value, as previously reported. For limestone samples this figure is again generally true, but occasionally a higher value of error is obtained (see Table VI).

TABLE V.

Sample.	Available Volume of Voids, c.cs.					Average Volume of Voids, c.cs.	Maximum Deviation from Average Vol. of Voids, c.cs.
	1.	2.	3.	4.	5.		
Sandstone							
I	4·61	4·60	4·57	4·56	4·56	4·58	+0·03
II	4·77	4·77	4·74	4·76	4·80	4·77	±0·03
III	4·03	3·99	4·01	4·01	3·99	4·01	±0·02
IV	4·05	4·06	4·07	4·03	4·04	4·05	±0·02
V	4·17	4·12	4·14	4·14	4·14	4·14	+0·03
Limestone							
I	4·39	4·45	4·40	4·42	4·48	4·43	±0·05
II	4·76	4·74	4·76	4·72	4·68	4·73	−0·05
III	5·20	5·25	5·24	5·29	5·24	5·24	+0·05
IV	5·03	5·00	4·99	4·98	4·97	4·99	+0·04
V	4·83	4·81	4·84	4·82	4·87	4·83	+0·04

TABLE VI.

Sample.	Available Porosity, per cent.					Average Available Porosity, per cent.	Maximum Deviation from Average, per cent.
	1.	2.	3.	4.	5.		
Sandstone							
I	25·4	25·3	25·2	25·2	25·1	$25{\cdot}2_5$	$\pm\ 0{\cdot}1_5$
II	25·0	25·1	24·9	25·0	25·2	$25{\cdot}0_5$	$\pm\ 0{\cdot}1_5$
III	25·6	25·3	25·5	25·5	25·4	$25{\cdot}4_5$	$\pm\ 0{\cdot}1_5$
IV	25·2	25·3	25·3	25·1	25·2	$25{\cdot}2_0$	$\pm\ 0{\cdot}1_0$
V	25·2	24·9	25·1	25·1	25·1	$25{\cdot}1_0$	$-\ 0{\cdot}2_0$
Limestone							
I	20·0	20·4	20·1	20·2	20·5	$20{\cdot}2_5$	$+0{\cdot}2_5$
II	21·9	21·9	21·9	21·8	21·5	$21{\cdot}8_0$	$-0{\cdot}3_0$
III	24·1	24·3	24·2	24·4	24·2	$24{\cdot}2_5$	$\pm0{\cdot}1_5$
IV	23·0	22·9	22·8	22·8	22·7	$22{\cdot}8_5$	$\pm0{\cdot}1_5$
V	22·0	21·9	22·1	22·0	22·2	$22{\cdot}1_0$	$-0{\cdot}2_0$

Thus only one result amongst fifty-five determinations differed by — 0·3 per cent., from the mean, whilst the average deviation was of the order of $\pm$ 0·1$_5$ per cent. It is safe to conclude that a figure for available porosity obtained as a mean value of three to five determinations by the liquid-absorption process on a sandstone or limestone sample may be reported

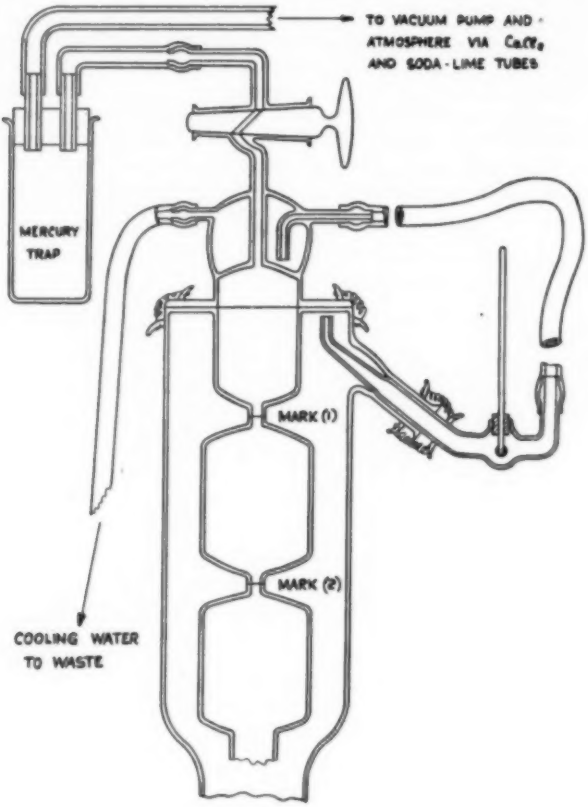


FIG. 2.

to the first decimal place, and be within an error from other mean values obtained by the same process not exceeding 0·2 per cent.

2. *Gas Expansion.*

The apparatus illustrated in Fig. 2 has been described previously, and also the method of operation detailed in Part II. The accuracy of the apparatus was found by using aluminium cylinders (the volume of which were known to $\pm$ 0·005 c.c.) to be $\pm$ 0·05 c.c. Thus in theory the accuracy of the apparatus as a porosimeter in conjunction with the pyknometer (Fig. 1) would fall on curve I, Fig. 3. As will be seen later, the actual accuracy

of the apparatus obtained with different values of bulk volume is approximately twice as great (curve II, Fig. 3). Thus to attain a mean value of available porosity which does not vary from any single determination by more than 0·25 per cent., a bulk volume of 32 c.c. is required theoretically, assuming the worst conditions operating. Actually volumes of 20 c.cs. and even lower values were sufficient to give this accuracy.

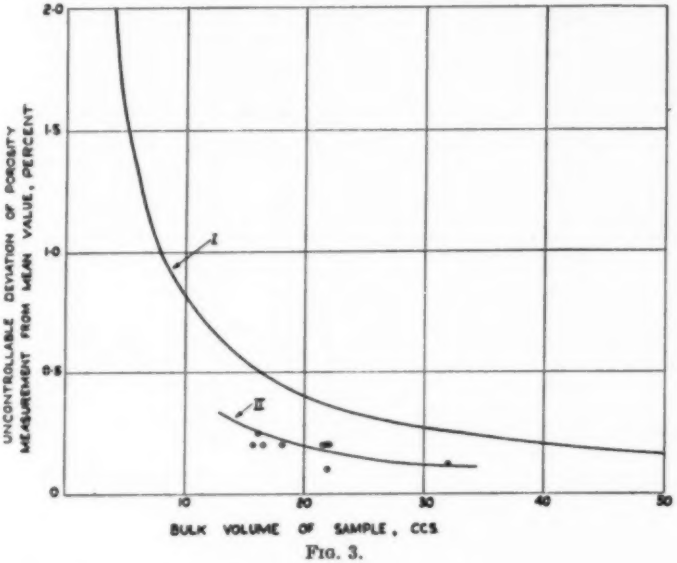


FIG. 3.

THEORETICAL AND ACTUAL MAXIMUM DEVIATIONS FOR VARIOUS VOLUMES OF SAMPLES.

Table VII gives details of a series of measurements of available volume using this apparatus. Four readings are taken for each calculation of a volume. It will be observed that the temperature of the water-jacket remains constant during an operation, which generally takes about five minutes to accomplish.

The apparent volume was calculated according to the formula :

$$v = V_1 - V_2\left(\frac{B-H}{H}\right) - V_c$$

where

v = apparent volume of sample in c.cs.
V_1 = volume of upper chamber in c.cs. = 64·14
V_2 = volume of second chamber in c.cs. = 175·12
B = barometric pressure in mm. Hg.
H = mercury head on expansion = h — 342·0 mm. Hg.
V_c = volume of container for sample in c.cs. = 2·59

the agreements and discrepancies in apparent volumes as measured by this method are given in Table VIII.

TABLE VII.

Sample:		Date:	Observer:	
Barometer, mm. Hg.	t_1 ° C.	h.	t_2 ° C.	$H = h - 342{\cdot}0$ mm. Hg.
751·75	15·2	927·9	15·2	585·9
751·80	15·1	928·0	15·1	586·0
751·85	15·1	928·0	15·1	586·0
751·85	15·1	927·7	15·1	585·7
Average 751·81				Average 585·9
751·80	15·1	928·0	15·1	586·0
751·70	15·2	927·9	15·2	585·9
751·75	15·2	928·0	15·2	586·0
751·75	15·2	928·0	15·2	586·0
Average 751·75				Average 586·0
751·75	15·2	927·8	15·2	585·8
751·70	15·2	927·9	15·2	585·8
751·75	15·2	927·9	15·2	585·9
751·75	15·2	927·9	15·2	585·9
Average 751·74				Average 585·85
751·75	15·2	927·9	15·2	585·9
751·75	15·2	927·9	15·2	585·9
751·75	15·2	927·9	15·2	585·9
751·75	15·2	928·0	15·2	586·0
Average 751·75				Average 585·93
751·70	15·2	928·0	15·2	586·0
751·72	15·2	927·8	15·2	585·8
751·75	15·2	927·8	15·2	585·8
751·70	15·2	927·9	15·2	585·9
Average 751·71				Average 585·88

TABLE VIII.

Sample.	Apparent Volume, c.cs.					Average Apparent Volume, c.cs.	Maximum Deviation from Average Apparent Vol., c.cs.
	1.	2.	3.	4.	5.		
Sandstone							
1	13·71	13·66	13·69	13·62	13·62	13·66	+0·05
2	11·96	11·95	11·95	11·89	11·89	11·93	±0·04
3	11·96	12·03	12·01	11·99	11·99	12·00	−0·04
4	12·46	12·40	12·43	12·41	12·41	12·43	±0·03
Limestone							
1	16·98	16·97	16·98	17·02	16·99	16·99	+0·03
2	16·80	16·76	16·77	16·75	16·72	16·76	±0·04
3	16·23	16·19	16·16	16·12	16·16	16·17	+0·06
4	16·86	16·84	16·83	16·82	16·81	16·83	+0·03
5	16·96	16·90	16·91	16·91	16·95	16·93	+0·03

The apparent volume of the voids or the difference between the bulk and apparent volumes, as found by the gas-expansion method, again tends to be more accurate than would be predicted assuming an additive nature for the errors. The volumes for the voids for nine samples are given in Table IX.

TABLE IX.

Sample.	Apparent Volume of Voids, c.cs.					Average Volume of Voids, c.cs.	Maximum Deviation from Average Vol. of Voids, c.cs.
	1.	2.	3.	4.	5.		
Sandstone							
1	4·42	4·47	4·44	4·50	4·50	4·47	−0·04
2	3·80	3·81	3·81	3·87	3·86	3·83	+0·04
3	4·11	4·04	4·06	4·07	4·07	4·07	+0·04
4	4·06	4·13	4·09	4·13	4·10	4·10	−0·04
Limestone							
1	4·97	4·97	4·94	4·88	4·90	4·93	−0·05
2	4·93	4·97	4·94	4·96	4·99	4·96	±0·03
3	5·46	5·43	5·48	5·51	5·49	5·47	±0·04
4	5·00	5·02	5·03	5·04	5·05	5·03	−0·03
5	4·96	5·02	4·99	5·00	4·95	4·98	+0·04

From the errors in volume of voids it is calculated that for a sample having a bulk volume of 20 c.cs. a mean value for porosity may be obtained by this apparatus having a maximum deviation from any one determination not exceeding ± 0·25 per cent. This is seen from Table X.

TABLE X.

Sample.	Available Porosity, per cent.					Average Available Porosity, per cent.	Maximum Deviation from Average, per cent.
	1.	2.	3.	4.	5.		
Sandstone							
1	24·4	24·5	24·5	24·8	24·8	24·6	±0·2
2	24·1	24·2	24·2	24·5	24·5	24·3	±0·2
3	25·6	25·1	25·3	25·4	25·4	25·3$_5$	±0·2$_5$
4	24·6	25·0	24·8	25·0	24·8	24·8	±0·2
Limestone							
1	22·6	22·7	22·5	22·3	22·4	22·5	±0·2
2	22·7	22·9	22·8	22·8	23·0	22·8	+0·2
3	25·2	25·1	25·3	25·5	25·4	25·3	±0·2
4	22·9	23·0	23·0	23·1	23·1	23·0	±0·1
5	22·5	22·9	22·8	22·8	22·6	22·7	±0·2

COMPARISON OF THE TWO METHODS.

1. *Accuracy.*

The two methods have been found to yield the same limits of accuracy in so far as reproducibility is concerned. Eight of the samples discussed

have been studied under strictly similar conditions and their porosities determined by both methods. The difference in bulk volume has already been noted to be of the order of 0·02 c.cs. when mean results are obtained by two workers on the same sample. Table XI compares the mean values for apparent volume and volume of voids as found by liquid-absorption and gas-expansion methods, each of the two mean values being found by a different observer.

TABLE XI.

Sample.	Mean Apparent Volume, c.cs.		Volume of Voids, c.cs.	
	Liquid Absorption.	Gas Expansion.	Liquid Absorption.	Gas Expansion.
Sandstone				
1	13·57	13·66	4·58	4·47
2	11·75	11·93	4·01	3·83
3	12·02	12·00	4·05	4·07
4	12·38	12·43	4·14	4·10
Limestone				
1	16·98	16·76	4·73	4·96
2	16·38	16·17	5·24	5·47
3	16·86	16·83	4·99	5·03
4	17·07	16·93	4·83	4·98

It was shown that each method of measuring apparent volume is accurate to $\pm$ 0·05 c.c., thus the maximum difference between the two methods should not exceed 0·10 c.c. Bulk volume measurement is accurate to $\pm$ 0·03 c.c. for the same worker. There is a discrepancy of 0·02 c.c. for different workers. Hence the worst agreement between the two methods as obtained by two workers for the mean values of volume of voids should not differ by more than 0·20 c.c., taking into account the effect of sources of constant errors, such as the volume of the glass container in the gas-expansion method and errors in the density of benzene in the liquid-absorption process. These errors will not appear in the reproducibility of the results, but will be evident on checking with another method not having these sources of error. Thus the disagreement in the available porosity value would add up to $\frac{0{\cdot}20}{20} \times 100 = 1$ per cent. in the extreme case for a bulk volume of 20 c.c.

More accurate agreements will generally be obtained as is shown by Table XII.

The errors in volume appear to be independent of size (within the limits studied), and better agreement will therefore be obtained in the values of apparent porosities on larger sizes than those selected. For a 40-c.c. sample the two methods would have a maximum difference of 0·5 per cent., since the maximum error on bulk volume would still be $\pm$ 0·03 c.c., and on available volumes $\pm$ 0·05 c.c., whilst the other errors discussed are also of constant nature.

TABLE XII.

Sample.	Bulk Volume, c.cs.	Mean Value for Available Porosity, per cent.		Difference, per cent.
		Liquid Absorption.	Gas Expansion.	
Sandstone				
1	18·14	25·2	24·6	0·6
2	15·76	25·4	24·3	1·1
3	16·07	25·2	25·3	0·1
4	16·52	25·1	24·8	0·3
Limestone				
1	21·7	21·8	22·8	1·0
2	21·64	24·2	25·3	1·1
3	21·86	22·8	23·0	0·2
4	21·91	22·1	22·7	0·6

2. *Time.*

The time taken for the preparation of the sample and its bulk measurement is identical for both processes. The time taken for apparent volume measurement is again approximately the same. The only difference in time is due to the necessity of drying the sample of benzene in the liquid absorption process before another measurement may be obtained—a period of 4 to 8 hours, depending on the size of the sample. This drying period is, of course, not required for the gas-expansion method.

When working with a minimum of five samples, the time taken for both processes is the same, if the working programme is staggered accordingly and five measurements are required for each mean value of porosity. Thus in the liquid-absorption process the porosity of five different samples may be measured once each in about 8 hours. To obtain the five mean values of the sample would require 5 days. In the gas-expansion process 1 day is sufficient to obtain the mean of five determinations for the porosity of one sample, and so again 5 days are required for five samples. The only advantage in favour of the gas-expansion method is the ability to obtain the mean value of each sample within a day of its preparation—*i.e.*, cutting, extracting and drying—whilst with the other method in order to work efficiently the mean value for all five samples may only be obtained after five days' work.

3. *Costs.*

The gas-expansion process requires an expensive barometer, glass instrument and triple distilled mercury and a rigid control for cleanliness from all the vapours of high vapour tension. The liquid-absorption process requires only an analytical balance, accurate weights and ordinary beakers. Thus the initial cost of the gas-expansion process is higher. Against this must be charged the running cost for the loss of pure dry benzene on each determination in the case of the liquid-absorption process, whilst the gas-expansion method requires the mercury only to be redistilled and apparatus recleaned after running the mercury through the lightly greased taps. The mercury becomes contaminated with grease, and air bubbles stick

to the glass sides even under vacuum after a definite period yielding erroneous, irregular results.

Conclusion.

Assuming experienced workers taking the necessary precautions :—

(1) The two processes discussed yield a mean value of five determinations for available porosity, having a maximum deviation from any single determination ranging from $\pm$ 0·25 to $\pm$ 0·10 per cent. for samples the bulk volume of which range from 20 to 40 c.cs. respectively.

(2) The maximum difference in the reported available porosity of samples as determined by the two processes and by two workers appears to be of the order of 1 per cent. for a bulk volume of 20 c.cs., and decreases proportionally with an increase in bulk volume.

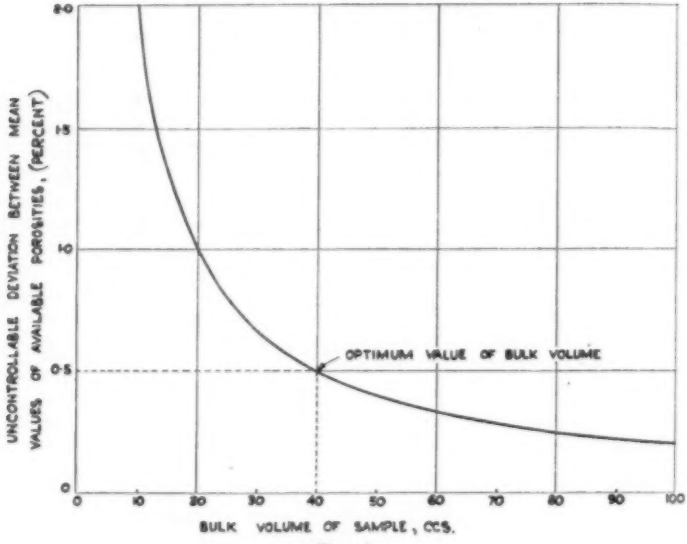


Fig. 4.

(3) To ensure the repetition of an available porosity determination to a maximum deviation of 0·5 per cent. between mean values obtained by different workers, employing each of the two processes on different days (*i.e.*, different barometric pressure, temperature, humidity, etc.) and using different pieces of apparatus (balances, weights, pyknometers, sample containers, etc.), the bulk volume of the sample should be at least 40 c.c. This value for bulk volume appears to yield the optimum value for accuracy, as further increase in volume entails difficulties (cutting, extracting, drying, gas-porosimeter manufacture, balances for mercury, etc.) far in excess of the relative increase in accuracy (Fig. 4).

(4) Should a lower figure for discrepancies be required, the bulk

volume of the sample should be in accordance with the value given on the graph in Fig. 4, and thus the cutter, extractors, drying-tubes, pyknometer and gas-expansion porosimeter should be so designed as to prepare and accommodate such a cylindrical sample. The balances should also be chosen capable of weighing the mercury used on calibration and accommodate the sample and beakers for the liquid absorption process.

(5) The time for a single determination of available porosity is greater for the liquid-absorption process by the period required to dry the sample subsequent to porosity evaluation. By staggering the working programme for several samples, the two processes may be made to give an equal number of mean values for available porosity in the same time.

(6) The sample does not appear to be affected by either of the two processes subsequent to available porosity determination.

The authors are greatly indebted to Mr. V. G. Norris, B.Sc., for assisting them throughout this investigation into Porosity.

Dept. of Oil Engineering & Refining,
University of Birmingham.

DETERMINATION OF THE ANILINE POINT OF DARK PETROLEUM PRODUCTS.*

By W. R. van Wijk and J. W. M. Boelhouwer.

Synopsis.

An apparatus for determining the aniline point of dark oils is described, using as a criterion the transparency to infra-red rays. Six samples can be tested simultaneously with this apparatus.

Introduction.

A general indication as to the chemical composition of a petroleum product is given by the temperature at which, on cooling down, a 50/50 (per cent. vol.) mixture of the oil and aniline begins to demix. This temperature is known as the aniline point of the oil.[1] With light oils the aniline point can be easily determined visually; with dark oils this is impossible, and special methods have to be used.

Such a method was developed by Leon Donn, which method consists in measuring the viscosity of a 50/50 mixture of oil and aniline at different temperatures, ranging from well above to well below the expected demixing point.[2] Owing to progressive demixing below the latter point, the variation of the viscosity with temperature in the lower range will be different from that in the higher range. Hence, the temperature *versus* viscosity curve will show a break at the temperature at which the second phase begins to separate—*i.e.*, at the aniline point of the oil.

In this way it is possible to determine the aniline point of even absolutely opaque oils.

In the *Journal of the Institution of Petroleum Technologists* one of us described a method for determining the cloud point of dark oils by measuring the transparency of such oils to infra-red radiation as a function of the temperature.[3] The same method can be used for determining the aniline point: at the demixing temperature the transparency of the mixture begins to change, owing to the appearance of the second liquid phase in a great number of droplets.

Although in principle the application of this method has to be restricted to oils which are not completely opaque to infra-red radiation, the practical significance of this limitation is very small. Even the aniline point of a fuel containing 7 per cent. by weight of hard asphalt could be measured, notwithstanding the fact that the transparency to radiation of 1·5μ wavelength of a layer of 1 mm. thickness of this oil was only 0·5 per cent.

As the method has proved to be very reliable and quick, a short description may be useful, the more so as, since the publication of the above-mentioned paper on the determination of the cloud point, an

* Paper received 22nd September, 1938.

improved apparatus has been developed, which makes it possible to carry out a number of determinations simultaneously in a short time.

The experimental procedure is as follows. The oil is mixed with the aniline at a temperature well above the expected demixing point. The mixture is then poured into a test jar, which is placed in a Dewar vessel, filled with a cooling liquid, and the whole is then placed between an incandescent lamp and a thermopile, the radiation from the lamp being focused into the oil by means of a lens, a second lens serving to focus the rays on to the thermopile. The liquid in the Dewar vessel is gradually cooled down, and the temperature of the solution in the jar is read. At each 1° C. fall in temperature the deflection of a galvanometer, connected to the thermopile, is read and plotted as a function of the temperature.

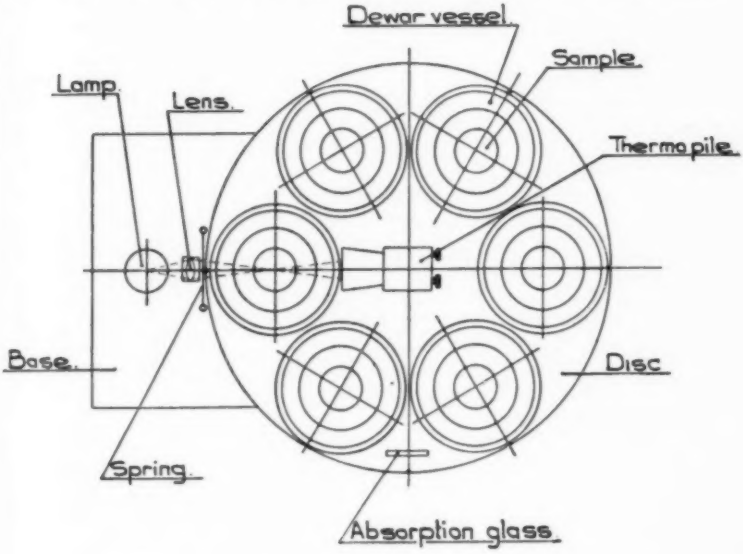


FIG. 1.

DIAGRAM OF APPARATUS.

A sharp break in the curve occurs at the temperature at which the aniline begins to separate.

EQUIPMENT.

In the case of the apparatus under consideration, six Dewar vessels are placed on a disc, which can rotate about a stationary thermopile located at the centre (Fig. 1). At a suitable distance from the thermopile an incandescent lamp is mounted on a common support (Fig. 1). By rotating the disc, the six samples can thus be successively interposed between the lamp and the thermopile.

Each test sample is contained in a jar closed with a rubber stopper carrying a thermometer. This jar is clamped in a holder and placed in a

Dewar vessel [4] in such a way as to allow the beam of radiation to pass under the mercury bulb of the thermometer.

If the sample is very dark, a test jar of 1 cm. diameter and about 10 cm. length is used, terminating in a flattened part of approximately 12 mm. height, so that a plane-parallel oil film of about 1 mm. thickness is obtained. The bulb of the thermometer rests on the flattened part. If the sample is not too dark, a normal test tube or a normal pour-point jar is used.

In order to obtain a suitable cooling rate (about 0·5 to at most 1·5° C./min.) the Dewar vessel is filled with a white oil in the case of samples having aniline points higher than about 50° C., and with carbon tetrachloride or alcohol in the case of samples having lower aniline points. The temperature of the cooling liquid is read on a second thermometer.

When starting from a comparatively high temperature—say, 130° C.—no special cooling is at first required for bringing down the temperature at a sufficiently rapid rate. At lower temperatures the liquid in the Dewar vessel is cooled by immersing in it metal cooling blocks, which are cooled in a separate vessel, filled with oil at much lower temperature. At temperatures below about 50° C., alcohol or carbon tetrachloride is preferred to white oil, as condensed water does not then tend to render the cooling liquid turbid.

The position of the sample relative to the thermopile and incandescent lamp is controlled by a spring with a pawl fitting into a vertical groove in the edge of the disc, so that when the latter is rotated, it naturally stops in a correct position.

Recording of the results is simplified in practice if all samples give the same initial deflection of the galvanometer. To this end, six series-resistances (one for each sample) are used, which are adjusted to give a deflection of the desired magnitude. The resistances are of a simple type, such as used in the better-class wireless sets; if the galvanometer damping allows it, a shunt may be used.

When the disc is turned, the resistance belonging to each sample is automatically switched in by means of a ring with contact points fixed to the disc, so that the electric circuit of the galvanometer and the thermopile is closed via the resistance belonging to a definite sample at the very moment that this sample is interposed between the thermopile and the bulb.

The source of light may be a normal motor-car bulb (say 6-v., 35-watt), the current being supplied by a storage battery of constant tension. In order that new bulbs need not be focused again, optically interchangeable bulbs of the so-called " pre-focused " type are used. The intensity of the radiation is controlled by means of an absorption glass (transparency about 25 per cent.), fitted on the disc, and can be corrected by a small resistance for any decrease of the battery tension, due to discharge. The thermopile is provided with a polished metal funnel. The irradiated surface is 0·8 cm.^{2}, and the sensitivity about 0·1 V. per W./cm.^{2} of energy entering the funnel.

The galvanometer has a sensitivity of 4μ V. per mm. deflection, and owing to the inertia of the system thermopile/series-resistances/galvanometer, it takes 3 seconds before the full deflection value is attained. The galvanometer is placed on a stand so that the thermometers and the galvanometer may be read simultaneously, thus permitting rapid and easy determinations. The photograph (Fig. 2) illustrates the equipment.

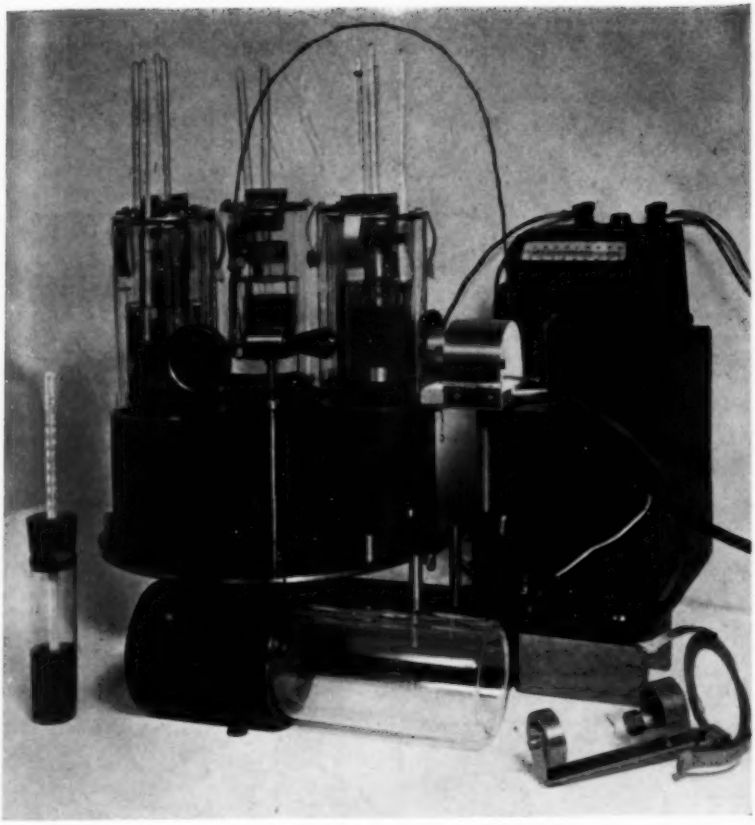


FIG. 2.

EQUIPMENT FOR THE DETERMINATION OF THE ANILINE POINT OF DARK PETROLEUM PRODUCTS.

[*To face p.* 600.

Results.

As a check on the method, first a number of transparent oils were investigated both by this method and by the normal visual method. In no case did the difference between the visual and the infra-red aniline point

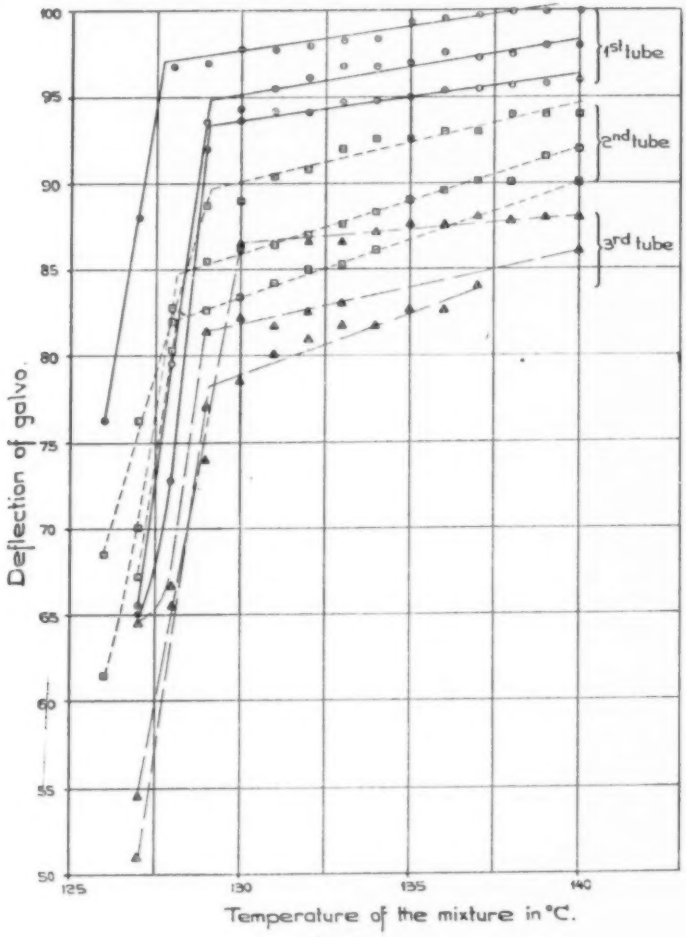


Fig. 3.

ANILINE POINT MEASUREMENTS WITH INFRA-RED LIGHT ON A CYLINDER OIL.

exceed 2° C. Since then the infra-red method has been in use for dark oils, giving full satisfaction.

From Figs. 3, 4 and 5, showing our measurements on three different types of oil, the accuracy obtained with the equipment described may be judged.

The galvanometer deflections, which are a measure of the transparency of the mixture, are plotted against temperature. Fig. 3 gives the transparency curves of a 50/50 (per cent. vol.) mixture of aniline and a cylinder oil; Fig. 4 relates to a gas oil, and Fig. 5 to an asphaltic fuel oil.

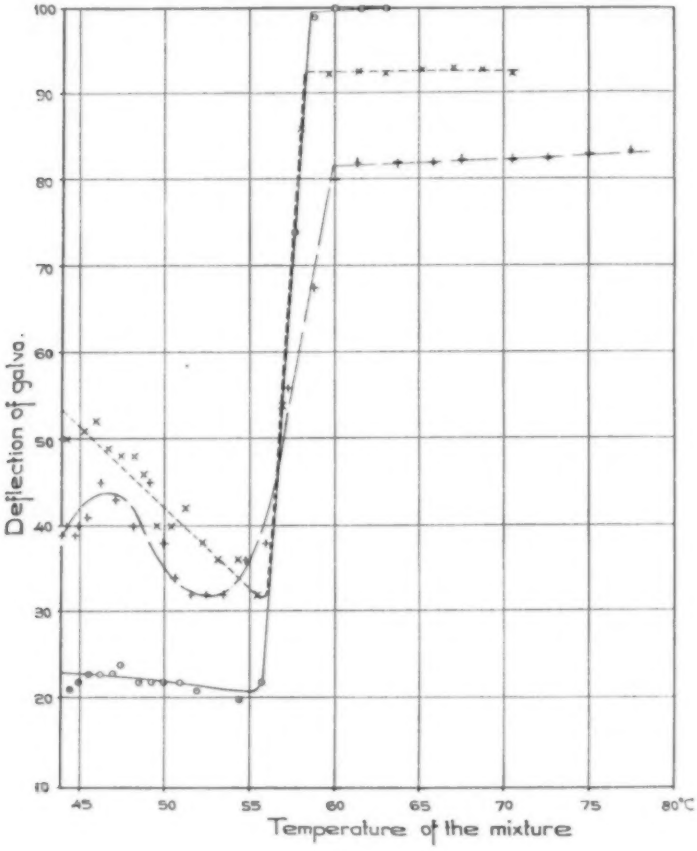


FIG. 4.

ANILINE POINT MEASUREMENTS WITH INFRA-RED LIGHT ON A GAS OIL.

A film of 1 cm. thickness of the cylinder oil still transmitted as much as about 8 per cent. of radiation of 1·5μ wave-length; in the case of the gas oil, however, and of the asphaltic fuel oil (which contained 7 per cent. by weight of hard asphalt), the film thickness was about 1 mm.; in these cases the films transmitted as little as 7 and 0·5 per cent. respectively of the radiation of 1·5μ wave-length.

Fig. 3 gives the transparency curve obtained in nine determinations,

and clearly shows the reproducibility of the tests. For the sake of clearness, the deflection curves have been shifted with respect to each other in

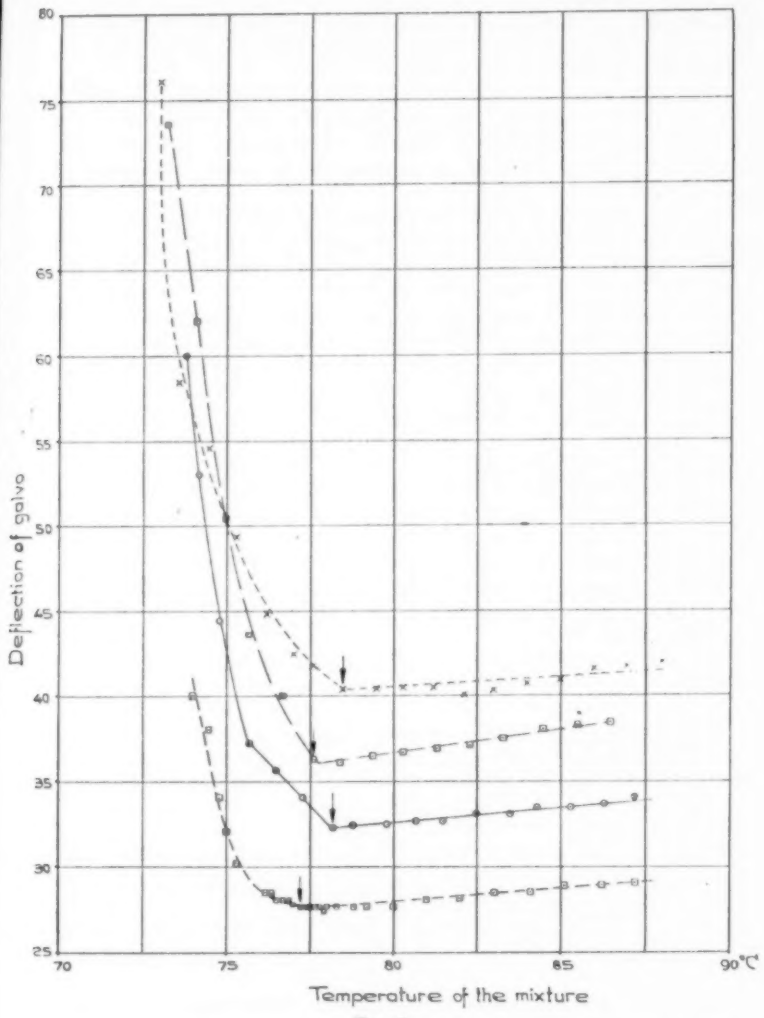


FIG. 5.

ANILINE POINT MEASUREMENTS WITH INFRA-RED LIGHT ON AN ASPHALTIC FUEL.

the vertical direction, so that for the second curve, for instance, the maximum deflection (100) has been plotted at the scale value 98.

The largest deviation between the single determinations is 3° C., inclusive

of inaccuracies due to differences in the composition of the aniline-oil mixtures.

The aniline point is 129° C.

In the tests on the gas oil and the asphaltic fuel oil, the aniline points found (59° and 78° C., respectively) do not differ by more than 2° C. in the duplicate determinations.

In all these measurements the cooling rate was approximately 1° C./min.

A very interesting point is the varying aspect of the curves. The cylinder oil is so highly transparent that the deflection of the galvanometer diminishes when the aniline phase separates in small drops, thus giving rise to turbidity.

The transparency of the gas oil decreases at first, but increases at a later stage owing to the aniline phase being much more transparent than the oil phase. Settling of the aniline will result in the formation of a bottom layer which is more transparent than the top layer. As the radiation passes through the bottom layer, an initial decrease must be followed by an increase in transparency. In the case of the nearly opaque asphaltic fuel oil, the difference in transparency between the oil layer and aniline layer is so pronounced that as soon as the aniline has begun to separate the transparency begins to increase, owing to very rapid coalescence of the droplets.

Full plots of the transparency curves of the above samples have been given for the purpose of illustrating the degree of accuracy obtainable with the improved apparatus. However, if an aniline point need only be determined to within about 3° C., it is unnecessary to plot the transparency curve, but instead the temperature may be noted at which the deflection of the galvanometer starts to change rapidly. This simplifies readings considerably, and even an untrained observer may handle six samples simultaneously.

The apparatus has also proved to be very suitable for the rapid determination of the cloud point of dark oils.

The authors are indebted to the Management of the N. V. De Bataafsche Petroleum Maatschappij for their permission to publish this paper.

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[1] For the definition of the aniline point of an oil, see I.P.T. method G.39 (T) in *I.P.T. Standard Methods*, 1935, pp. 215–217.
[2] Leon Donn, "Determining the Aniline Point of Dark Petroleum Products," *Ind. & Eng. Chem. Anal. Ed.*, 1937, **9** (5), 202.
[3] W. R. van Wijk, "Determination of the Cloud Point of Dark Oils," *J. Inst. Petr. Techn.*, 1936, **22**, 754–760.
[4] For a description of a suitable holder, see the paper given under Reference 3.

Laboratory of N.V. de Bataafsche Petroleum Maatschappij
(Royal Dutch Shell Group),
Amsterdam.

A LABORATORY METHOD FOR EVALUATING CRUDE OIL, WITH SPECIAL REFERENCE TO TRINIDAD CRUDE.*

By R. Edgeworth Johnstone, M.Sc., F.I.C., and R. Palmer, M.A.

The purpose of this paper is to describe a simplified laboratory procedure for evaluating crude oil in terms of three fractions: gasoline, gas oil and fuel oil, so as to give, in addition to the yield figures to be anticipated from topping operations, quantities of the gasoline and gas-oil fractions sufficient for determining the octane rating of the gasoline and the ignition quality of the gas oil. It is scarcely necessary to say that to-day the knock-rating of a gasoline, as determined by the C.F.R. testing engine, is one of its most important properties. Furthermore, in view of the increasing demand for high-octane aviation spirits, the refiner must keep well informed concerning both the octane rating of the gasoline stocks at his disposal and their response to tetraethyl lead.

Similarly, standard methods are being worked out for the classification of diesel fuels in terms of cetane number, and it is clear that refiners must be prepared to furnish regular supplies of diesel fuels meeting ignition quality specifications.

It is therefore essential that the method of evaluation adopted should give the fractions required, with properties closely similar to those of the corresponding plant products, in amounts sufficient for engine tests. Further, it is desirable that these distillates be obtained by means of a single distillation, and that the apparatus should be comparatively simple and suitable for routine use, so that it may be readily applicable to samples from new wells, samples from wells the crude of which has changed in quality, and samples of bulk crude oil offered for purchase, etc.

The standard crude evaluation methods at present available do not satisfy the above requirements. We may consider first the methods given in the I.P.T. Standard Methods Book, designated by the serial numbers C.P.3 and C.P.3a. In Method C.P.3 the volume of crude oil taken for testing is only 100 ml., so that very small yields of distillates are obtained. The method prescribes that distillation shall be continued up to a vapour temperature of 300° C., but under these conditions severe cracking in the flask is liable to occur. Experiments have shown that in some cases the yields of gas oil given by Method C.P.3 have been more than twice those given by either steam or vacuum distillation.

Method C.P.3a relates to the distillation of crude petroleum on a larger scale, but cannot be regarded as a standard method, as it consists of only a set of very general suggestions. As there is no strict specification of a standard apparatus, quantity of oil to be tested, etc., the recommendations made can only be considered as a general outline of the procedure to be

* Paper read at a General Meeting of the Trinidad Branch held at the Pointe-a-Pierre Club, on May 11th, 1938, Mr. E. C. Scott in the Chair.

followed. The maximum vapour temperature is fixed at 275° C., with a liquid temperature not to exceed 320° C. On the basis of work done by the authors, these temperatures are considered too high, for, owing to local overheating in the distillation flask, some cracking is liable to take place.

Referring now to A.S.T.M. standard methods, the A.S.T.M. Method D.285 specifies in detail a method for a distillation to be carried out on a 300-ml. sample, employing a Hempel distillation flask, but this method is only intended for the preparation of a naphtha sample from the crude oil, and only permits the making of a distillation test on the naphtha sample obtained.

Regarding other methods which have been used, the "Four-point control" method developed by the Standard Oil Company of California [1] was intended primarily for estimating the percentage of U.S. motor gasoline in California crude oils. A double distillation of the gasoline–kerosine fraction is involved, also a separate vacuum distillation of the residue if heavier distillates are required—*i.e.*, three distillations would be made on each crude-oil sample, and the quantities of distillate obtained would probably be insufficient for engine tests.

In U.S. Bureau of Mines Bulletin 207 [2] a method of distillation is described which has since been fairly extensively used in the examination of crude-oils. The flask is of the Hempel type, similar to, but not identical with, that specified in the A.S.T.M. Method D.285. A 300-ml. sample of crude oil is taken and distilled, first at atmospheric pressure, then under vacuum; consequently the yields of distillates are small. For the vacuum distillation a different kind of column packing is described, hence two separate distillations are necessary. In the same publication various large types of distillation apparatus are described, but none of these appears to have been generally adopted.

This survey of existing standard methods indicates that there is at present no generally accepted procedure by which a crude oil can be conveniently and reproducibly evaluated in terms of the yield, A.S.T.M. distillation and knock-rating or ignition quality of the distillates obtained. Moreover, certain of the present methods may permit cracking to occur during the distillation of the gas-oil fraction, seriously affecting both the yield and quality of the distillate obtained and the residual fuel oil.

In these circumstances the authors have found it necessary to develop for refinery-control purposes a method to meet the described requirements.

To prevent cracking, it is obviously essential to use steam or vacuum in distilling the gas-oil fraction. Vacuum distillation was chosen because of the greater certainty with which the observed temperatures may be converted into the corresponding atmospheric boiling points.

The method finally adopted may be briefly summarized as follows:—

A 4-litre sample of the dried crude oil is distilled in a Hempel-type apparatus up to a vapour temperature of 195° C., obtaining a 200° C. F.B.P. light fractions distillate. A specified controlled vacuum is then applied and the distillation continued, gas-oil fractions being taken off in approximately 5 per cent. cuts up to a specified maximum vapour temperature. Aliquot portions of the fuel-oil residue and the 5 per cent. gas-oil fractions are then successively blended back for viscosity tests, until a

blend is obtained with viscosity less than 150 seconds Saybolt Furol at 122° F. The amount of gas oil required to give a fuel oil of the standard 150 seconds Saybolt Furol viscosity is then determined by linear interpolation, and the balance taken as the gas-oil yield.

The quantity of sample distilled ensures that in most cases there is sufficient of the gasoline and gas-oil distillates for A.S.T.M. distillation and engine tests. Not more than 6 hours are occupied in making the distillation test, so that the method is suitable for regular laboratory use.

A detailed description of the evaluation method is given in the Appendix.

Results.

Following are typical examples of the results of duplicate distillations made on samples of various types of crude oil, and it is considered that the degree of accuracy indicated is satisfactory for normal evaluation requirements :—

Crude Sample.	Dry Crude Analysis, Vol.			Octane Number of Light Fractions. C.F.R. Motor Method. A.S.T.M. D357–37T.	Aniline Point of Gas Oil, ° C. I.P.T. F.O. 23.	Specific Gravity of Fuel Oil.
	Light Fractions.	Gas Oil.	Fuel Oil.			
A	29·4	26·1	44·5	55·9	56·5	0·9532
	29·9	25·3	44·8	56·2	56·6	0·9534
B	18·6	12·0	69·4	63·8	46·5	0·9612
	18·9	11·2	69·9	63·5	46·5	0·9620
C	18·0	20·4	61·6	66·4	41·4	0·9739
	18·8	20·6	60·6	66·5	41·5	0·9757
D	21·3	19·2	59·5	64·6	42·0	0·9692
	20·8	18·6	60·6	64·3	42·1	0·9789

Although this testing procedure is applicable to all crude oils, members of this Branch will be interested in some of the results obtained on Trinidad crudes, and in the use of the method in local refining operations.

In general, Trinidad crudes contain about 17–21 per cent. of light fractions, having 10–17 per cent. distilling at 100° C., and with octane number, C.F.R. Motor Method, ranging from 61 to 68. Other local crudes more paraffinic in character may contain as much as 30 per cent. light fractions with an octane number as low as 55.

For the bulk of Trinidad crude oil, the gas-oil content ranges from 16 to 21 per cent., as measured by the evaluation method, this gas oil having approximately 280–320° C. end-point, with aniline point about 42° C. and cetane number 36. Crude from certain wells, however, is deficient in gas oil to the extent that after removal of light fractions the viscosity of the fuel-oil residue is in excess of 150 seconds Saybolt Furol at 122° F. Such fuel oil must have gas oil added to it to reduce it to the standard viscosity, and for proposed purchases of crude oil of this type,

the method affords an easy means of computing how much gas oil is required.

With regard to fuel oil, the average Trinidad crude contains between 55 and 65 per cent. of 150 sec. fuel oil, of approximately 0·97 specific gravity. Certain paraffinic types, it may be noted, have as low as 40 per cent. of fuel oil, with specific gravity as low as 0·953. In this connection the authors wish to make it clear that the selection of what is to be considered standard fuel oil is purely arbitrary. The standard of 150 seconds Saybolt Furol viscosity at 122° F. referred to in this paper was chosen to meet the operating requirements of a particular refinery, topping crude oil to a standard fuel of this quality. Other purchasers or refiners may lay down their own standard fuel-oil specifications, written in terms of either the Furol or Redwood viscometers, or in terms of other appropriate fuel-oil tests.

Regarding the use of the method in refinery control, members of this Branch will readily appreciate its application to local conditions, the position being that three refineries process the bulk of the crude oil produced from a large number of different fields. These crudes differ to such an extent that it is generally necessary to segregate the different types and to process them separately through the refinery for the manufacture of particular products. A reliable evaluation method of the type described is obviously essential to proper control and maximum economy in the topping stage of the refinery operations, and this method constitutes a suitable basis for the preparation of estimates covering the future production of various products and of the quality of these products in terms of the standard petroleum tests. Furthermore, it affords an excellent check on the quality of current crude-oil production, through the medium of tests on monthly bulk samples from the different sources of supply. In studying new production, the properties of crude from new horizons may be readily correlated with those of crude oil from other wells in the same field or wells in other fields. Another and particularly important use of the method is that it serves as a rational basis for crude-oil purchase agreements, in that the prospective purchaser may readily assess the value of the crude oil in terms of the value of its component fractions.

One further point of interest may be noted, regarding a useful extension of the method in connection with the production of aviation spirit. In testing crude oil to be segregated for aviation-spirit manufacture, two separate gasoline cuts may be taken in the atmospheric distillation: first, an aviation-spirit cut of the desired volatility—say, 50 per cent. distilling at 100° C.—and secondly, a heavy naphtha. Examination of the properties of these two cuts gives data required for process control in aviation-spirit manufacture and in the reforming of the naphtha cut.

The authors hope, in bringing the method described in this paper to the notice of the Institute of Petroleum, that it may perhaps form the basis of a new I.P.T. standard method for the distillation of crude petroleum more in accordance with modern requirements than the existing standard methods. In conclusion, the authors wish to state that during the last year, over which period crude evaluation methods have been studied, Mr. P. B. H. Trasler and Mr. A. E. Gerty have rendered valuable assistance in developing the method described, and the authors' thanks

are due also to Messrs. Trinidad Leaseholds, Ltd., for their kind permission to publish this paper.

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[1] H. G. Vesper, *Industr. Engng Chem.*, **18**, 64, 1926.
[2] U.S. Bureau of Mines Bulletin 207, "The Analytical Distillation of Petroleum and its Products," E. W. Dean, H. H. Hill, N. A. C. Smith and W. A. Jacobs.
[3] *Industr. Engng Chem.*, September 1915. Suitable receivers may be obtained from A. H. Thomas & Co., Philadelphia, Pa., U.S.A.
[4] E. S. L. Beale and P. Docksey, *J. Inst. Petr. Tech.*, 1935, **21**, 860.

APPENDIX.

Part I. Definition of Products.

For the purposes of the evaluation, crude oil shall be considered to be a mixture of:—

(*a*) Light Fractions. All that portion distilled from the crude having an A.S.T.M. final boiling point of 200° C.
(*b*) Gas Oil. All distillate products between light fractions (*a*) and the standard fuel oil (*c*), removed from the topped crude under the specified conditions.
(*c*) Fuel Oil. That portion of the crude remaining after removal of light fractions (*a*) and gas oil (*b*), conforming to the following specifications:—

Viscosity Saybolt Furol at 122° F., sec. max.	150
Flash point, P.M. ° F., min.	150

(*d*) Water and Sand. Water, sand or other foreign matter.

Part II. Apparatus.

(1) *Distillation Flask.*

The distillation flask shall be constructed from $\frac{1}{16}$-in. mild-steel sheet, and all joints shall be welded. The flask is illustrated in Fig. 1, which also gives dimensions and tolerances.

(2) *Fractionating Column.*

The fractionating column, illustrated in Fig. 2, shall be made from $1\frac{1}{2}$-in. I.D. mild-steel standard pipe. To the lower end of the column shall be welded a 5-in. flange, drilled with four holes as shown in the figure. At $2\frac{1}{2}$ in. from the upper end a vapour tube, also of mild-steel pipe, $\frac{3}{8}$-in. I.D., shall be welded at an angle of 60°. To provide a support for the packing, two brass strips $\frac{1}{4}$ in. wide and $\frac{1}{32}$ in. thick, at right angles to one another, shall be brazed to the bottom of the column. All dimensions and tolerances are given in Fig. 2. The column shall be packed with $\frac{1}{4}$-in. lengths of $\frac{1}{4}$-in. glass tubing, resting on the brass strips and extending to 1 in. below the bottom of the vapour outlet tube at its junction with the fractionating column.

The vertical sides and the top of the distillation flask and the column shall be thoroughly lagged with a single layer of $\frac{1}{4}$-in. asbestos cloth, special care being taken to lag the flange properly. In addition, the column shall be wound with a single layer of $\frac{1}{4}$-in.-diameter asbestos cord.

(3) *Condenser.*

A glass jacket of the Liebig type, 15–18 in. long, shall be fitted over the vapour tube, the combination of jacket and vapour tube forming the condenser. Provision shall be made to circulate cooled water through the condenser whenever necessary.

(4) *Receiver.*

The end of the vapour tube shall be connected by means of a tightly fitting cork to a fractional receiver of the Bogert type (Fig. 3).

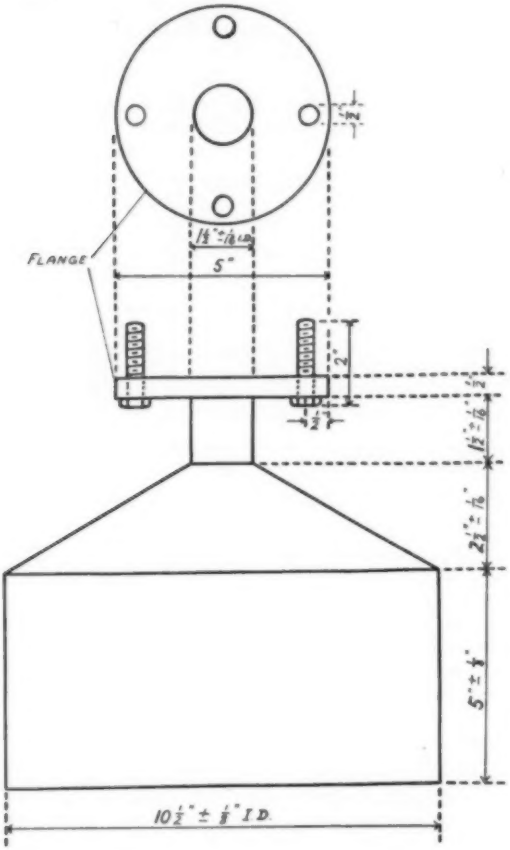

FIG. 1.

STANDARD DISTILLATION FLASK.

Material of flask $\frac{1}{16}$ in. mild steel sheet all welded (except flange botts).

(5) *Vacuum Pump.*

A vacuum pump, capable of maintaining on the system a pressure of 20 mm. of mercury, shall be connected to the receiver.

(6) *Thermometer.*

The I.P.T. or A.S.T.M. low-distillation thermometer, 0–300° C., shall be used.

(7) *Support.*

Any suitable support may be used, but an iron ring approximately 9 in. in diameter and 10–12 in. high is preferable.

(8) *Source of Heat.*

Either a gas-burner or an electric-heater, adequate for the specified distillation rate, may be used, but a gas-burner fitted with a sensitive regulating valve is more convenient.

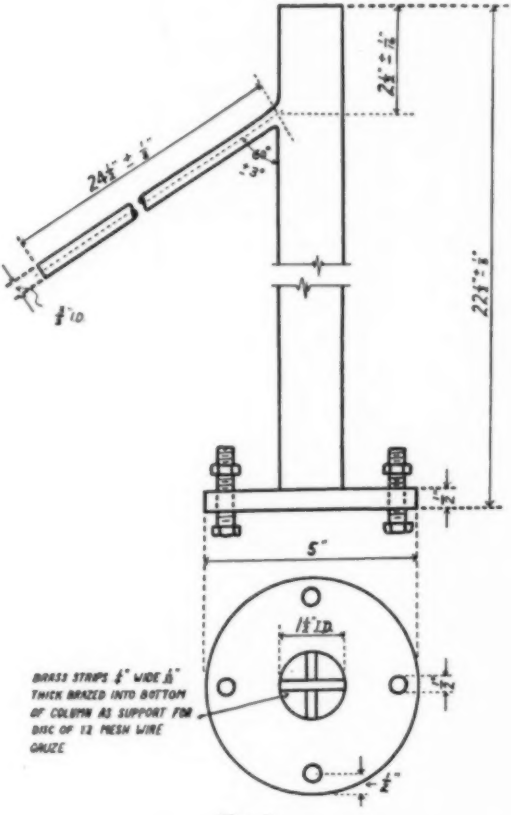

FIG. 2.

FRACTIONATING COLUMN FOR STANDARD CRUDE OIL FLASK.

(9) *Shield.*

A suitable shield shall be provided for the flask and column unless the distillation is carried out in a room free from draughts. When gas-heating is employed, a sheet-metal cylinder lined with asbestos may be used, projecting 5 in. above the ring on which the flask rests. With this type of shield, fitted closely to the vertical sides of the flask, the sides of the latter need not be lagged.

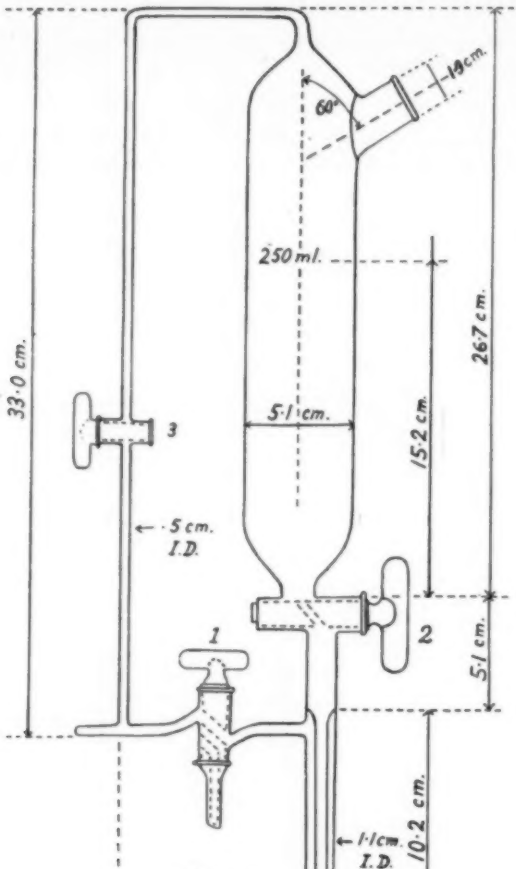

FIG. 3.

FRACTIONAL RECEIVER.

Dimensions are approximate only. Receiver is graduated each 5 ml. up to 250 ml.

(10) *Measuring Graduates.*

Accurate graduates of suitable capacity, which can be tightly stoppered, shall be used.

Part III. Procedure.

(a) *General.*

The specific gravity of the crude as received shall be determined. The flask shall be weighed, cooled, and 4 litres of crude oil previously cooled to 55° F. or lower shall be

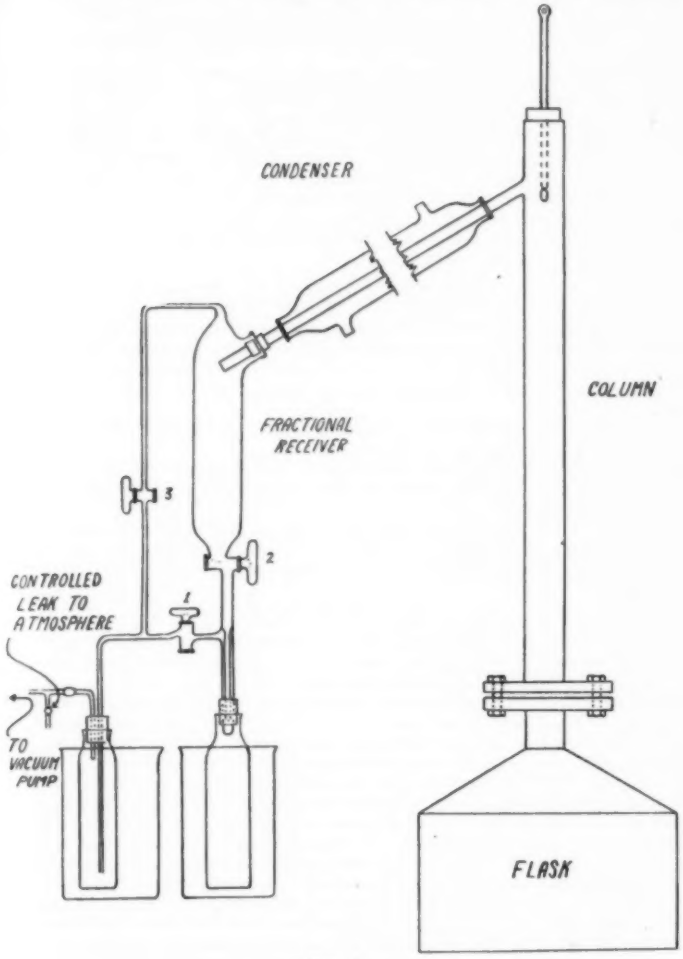

Fig. 4.

ARRANGEMENT OF APPARATUS.

measured into it, care being taken to avoid any spilling on the flange or outside of the flask. The flask and contents shall then be weighed, all weighings being recorded to the nearest gramme.

When the crude oil contains more than 1 per cent. of water the oil must be dried prior to distillation, to prevent priming. For this purpose 1½–1½ gal. of the crude oil shall be agitated thoroughly with calcium chloride in a tightly stoppered 2-gal. can, and allowed to stand over-night at room temperature. Commercial fused calcium chloride, screened to remove all powder, and passed through a sieve of ¼-in. mesh, should be used in the proportion of 3 gm. of calcium chloride per millilitre of water to be removed. After checking the moisture content of the dried oil, the crude shall be cooled to 55° F. and the specific gravity determined on a small portion. Four litres of the oil shall then be filtered through a 30-mesh screen into the flask, and the whole reweighed.

Immediately afterwards the fractionating column shall be bolted tightly to the distillation flask, using a Permanite or other suitable gasket smeared with graphite paste, and the whole apparatus connected up as shown in Fig. 4. A suitable measuring graduate cooled in a bath of crushed ice and water shall be connected with a tight-fitting cork to the outlet of the Bogert receiver, and this graduate shall in turn be connected to the second cooled receiver illustrated in Fig. 4. The top of the column shall be fitted with a tight-fitting cork carrying centrally the 0–300° C. thermometer so adjusted that the lower end of the capillary is ½ in. below the lower edge of the side tube at its junction with the column. The cork shall be sealed with a paste of litharge and glycerine, or other suitable material.

(*b*) *Determination of Light Fractions.*

This determination shall be carried out at atmospheric pressure. Heat from a suitable source shall be applied to the flask, and the heating so regulated after distillation commences that a distillation rate of 8–10 ml. per minute is maintained throughout.

During this distillation stopcocks 1 and 2, Fig. 3, shall be open and stopcock 3 closed.

Cooling water at a maximum temperature of 25° C. shall be made to circulate through the condenser during the whole distillation.

Distillation shall be continued until a vapour temperature of 195° C. is indicated by the thermometer, when heating shall be stopped and the condenser allowed to drain for at least 2 minutes.

The distillate comprises the light fractions, together with any small amount of water which may have been present in the crude-oil charge. The light fractions and water, if any, shall be carefully measured and the temperature at the time of measurement recorded.

(*c*) *Determination of Gas Oil and Fuel Oil.*

This determination shall be carried out at a pressure of 20 mm. ± 3 mm. of mercury, which can be easily maintained by means of a controlled air-leak, or by one of the well-known arrangements for vacuum control.

After removal of light fractions and water at atmospheric pressure, the flask and its contents shall be allowed to cool down for 15–20 min. A suitable receiver which need not be immersed in a cooling bath shall be connected to the Bogert-type receiver, and evacuation shall then be started slowly using a leak to atmosphere. When the specified pressure is obtained, heat shall be applied carefully to the flask. Attention to this procedure will eliminate any difficulty due to priming. Distillation shall be carried out at a rate of 8–10 ml. per minute, and each 5 per cent. fraction, based on the crude charge, shall be collected separately. For the collection of these fractions, a separatory funnel may be substituted for the graduated cylinder attached to the Bogert receiver.

The distillation shall be continued to such a point that the fuel-oil residue in the flask is heavier than the specification requires, or until the vapour temperature reaches 220° C. In no case shall the vapour temperature as indicated by the distillation thermometer exceed 220° C. This is equivalent to a maximum vapour temperature of 350° C. at atmospheric pressure. Temperature measurements have shown that for this maximum vapour temperature of 220° C. the liquid temperature in the distillation flask will normally not exceed 300° C. During the distillation, water at a temperature of 25–35° C. shall be circulated through the condenser. Warmer water may be used towards the end of the distillation if found necessary to keep the distillate sufficiently fluid.

On completion of the distillation the condenser shall be allowed to drain for at least

2 min. When the apparatus is sufficiently cool, the flask shall be disconnected, all lagging removed, and the flask and residuum weighed. Specific gravity and viscosity determinations shall be made on the residue in the flask.

(d) Determination of Water Content and Sand Content.

The water content of the crude-oil sample as received shall be determined by the A.S.T.M. Method D.95.

For the determination of sand, a 500-ml. sample of the crude oil as received, of known temperature and water content, shall be diluted with naphtha or kerosine and filtered through a gravimetric filter-paper of known ash content. The filter-paper shall be washed with kerosine until completely free from crude oil, allowed to drain and ignited in a tared platinum crucible. The nett weight of ash obtained shall be taken as the weight of sand in the crude-oil sample. This weight shall be converted into a volume figure, assuming a specific gravity for sand of 2·5, and the result expressed as a percentage by volume of dry crude oil.

Part IV. Calculation of Results.

All volumes shall be corrected to volume at 60° F., in accordance with the latest revised issue of either Bureau of Standards Circular C410 or the Standard Abridged Volume Correction Table for Petroleum Oils, A.S.T.M. Standard D.206.

For commercial purposes it is desirable to record the evaluation results, first in terms of the crude oil free from water and other foreign matter, secondly in terms of the wet crude oil sample as received.

(a) Dry Crude Analysis.

All fractions shall be expressed as a percentage by volume of the dry, sand-free crude oil.

When water is present in the crude-oil charge, the observed specific gravity shall be corrected to the specific gravity of dry crude before the volume is calculated, the weight of dry crude oil charge in grammes being taken as the total weight of charge in grammes, less the weight of sand and less the volume of water in millilitres received with the light fractions—*i.e.*, the specific gravity of the water is taken as 1.

The measured volume of light fractions shall be corrected to volume at 60° F., and expressed as a percentage by volume of dry crude. This figure is then adjusted for distillation loss as indicated in the final paragraph.

The volume of the residue remaining in the flask on completion of the distillation shall be calculated, and a deduction made for sand content. An aliquot portion of it shall then be blended back with a corresponding portion of the heaviest vacuum distillate—*e.g.*, 10 per cent. of the residue would be blended with 10 per cent. of the heaviest vacuum distillate. Specific gravity, viscosity and flash-point of the blend shall be determined.

A second aliquot portion of the residue shall be blended with the corresponding portion of a 50 : 50 mixture of the last two vacuum distillates and specific gravity and viscosity of the blend determined.

Similar proportional blends of residue with mixtures of equal volumes of the last three, last four, etc., vacuum distillate fractions shall be made until the blend is in accordance with the required specification.

The minimum amount of blended residue agreeing with the specification shall be determined by interpolation. This minimum amount, less the calculated volume of sand, shall be expressed as a percentage by volume of dry crude and reported as fuel oil.

The amount of gas oil which would be required to be added back to the total residue obtained shall be calculated. This calculated amount shall be deducted from the total volume corrected to 60° F. of all the gas-oil fractions received, and the remaining volume, expressed as a percentage of the dry crude oil charged, shall be reported as gas oil.

The difference between 100 and the sum of the percentages of light fractions, gas oil and fuel oil, is loss and error. If this exceeds 3·0 per cent. the evaluation is to be repeated. Loss and error not exceeding 3·0 per cent. is to be added to the light

fractions figure. The analysis of the dry crude oil will then be as shown in the following example :—

Water in original sample	2·5
Sand in original sample	None
(Distillation loss, included in light fractions	0·9)

Dry Crude Analysis.

	Volume % of Dry Crude.
Light Fractions, including loss	28·35
Gas Oil	33·84
Fuel Oil	37·81
	100·00

(*b*) *Wet Crude Analysis.*

For the purpose of evaluating the crude oil in terms of the crude-oil sample as originally received, the analytical figures calculated as set out in the preceding Part IV (*a*) are expressed as percentages by volume of the original wet crude oil. Using the example given in Part IV(*a*) the crude-oil analysis would be reported as follows :—

Wet Crude Analysis.

	Volume % of Wet Crude.
Light Fractions	27·64
Gas Oil	32·99
Fuel Oil	36·87
Water	2·50
Sand	None
	100·00

PART V. ANALYSIS OF PRODUCTS.

All required tests on fractions shall be made according to the latest revised I.P.T. or A.S.T.M. methods, as conditions require.

Light Fractions.

The usual distillation points, percentage recovery at 100° C., and final boiling point shall be reported.

Gas Oil.

A bulk sample shall be made from the fractions obtained, due allowance being made for that portion, obtained by interpolation, required to be added to the residue to give the specified fuel oil. All tests required shall be made on this bulk sample.

Fuel Oil.

The properties of the standard fuel-oil residue shall be determined by interpolation of the test results on the blends made, unless special analytical tests are required.

DISCUSSION.

Mr. A. G. V. BERRY : The authors are to be congratulated on a successful attempt to devise a system of crude-oil testing applicable to Trinidad crudes which generally yield products with high specific gravity for a given boiling point, and furnishing data on the products in line with modern requirements.

Some crudes from other parts of the world are resolved into products of

quite different characteristics, but there does not appear to be any fundamental difficulty in modifying the cutting conditions to suit all types of crude. Obviously the refiner and the producer are both concerned in getting the maximum return from the crude oil, which is only another way of saying that the given crude must be cut to give the maximum proportions of the more valuable fractions that it is capable of yielding, which in turn depends on the quality of each product.

The proposed method of evaluation is fair to both producer and refiner, in that payment is made on the basis of the yields of products actually obtained in the refinery from that crude, and not on some arbitrary temperature cut for gas oil which might or might not give a commercial fuel oil.

It appears to me that there might be some difficulty in obtaining complete condensation of the light fractions with a condenser jacket only 15–18 in. long when the permissible rate of distillation is 8–10 ml. per minute, unless the cooling water circulated is kept considerably below the specified maximum of 25° C. The paper does not indicate the actual losses normally found. Although the losses are considered as light fractions and are added to the actual yield obtained—which is quite reasonable—nevertheless it is desirable to reduce the loss to a minimum, in view of the effect of losses on the tests for quality, and for this reason I would suggest that the maximum permissible temperature for cooling water should be 15° C., which is always easily attainable.

Again, in reference to light fractions which for Trinidad purposes are cut at 195° C. for gasoline of 200° C. A.S.T.M. end-point, it is quite conceivable that a crude oil deficient in very volatile fractions would yield a product of higher end-point by A.S.T.M. test than another crude rich in volatiles, each being cut at 195° C. Is it the intention of the authors that the cut at 195° C. shall be the criterion of yield, or is it proposed that some correction should be made for the amount of yield between the end-point determined and a standard end-point of 200° C.? It is purely arbitrary, but this point should be dealt with and clearly stated, especially in purchasing agreements, to avoid possible misunderstanding in view of the price differential between gasoline and gas oil. For refinery control the point is only of academic interest.

The idea of reducing the effects of cracking the crude in producing gas oil appeals to me, as only by this means can the evaluation of heavy crudes be carried out under reproducible conditions, and the proposed means of doing so are very practicable.

Mr. MELVILL: Mr. Berry's remarks just reminded me of one criticism which I think can be levelled at this paper. The authors, I think, fix the maximum losses at 3 per cent., which figure appears to me unduly high, because 3 per cent. loss on a crude containing 20 per cent. of gasoline means 15 per cent. on the gasoline.

I suggest that this high loss is probably due to the inadequacy of the condenser

Mr. A. H. RICHARD congratulated the authors on a valuable contribution. The speaker had found the same difficulty with existing standards,

and would support the suggested standardization, subject to certain modifications.

The scale of the authors' apparatus was designed for a particular oil and for the particular condition of refinery control.

The light fractions content of oils will naturally vary in different localities and countries, and the test will not always be required for refinery control. For a solely producing company the scale was bigger than necessary to obtain comparative data on oils from individual wells.

The speaker therefore felt that in its present form the proposed test was unlikely to meet with sufficient general approval for adoption as a standard, and that this same difficulty had so far to a certain extent militated against standardization.

He had started experiments himself some time ago, and after trying various forms of apparatus, reached the conclusion that the best line of attack would be to model a test on the A.S.T.M. Method D.285, which, with its half-brother, the Bureau of Mines Method, appeared to be most widely used.

The speaker found that by retaining the same type and dimensions of column, but with a larger flask, results in agreement with the A.S.T.M. Method D.285 were obtained. It was essential, however, to design the flask so that the distance between the oil surface as filled and the bottom of the column packing—which is in effect part of the fractionating height—was the same in both cases. For this purpose the top of the flask should be formed with a slight dish—¼ in.—instead of the conical section shown by the authors.

This appears to open up the possibility of developing a standard column which will give concordant results with a range of three or four standard flasks to satisfy all requirements—say of 300, 1000, 2000 and 4000 ml. capacity.

The speaker was prepared to give the fullest possible co-operation in evolving a standard test along these lines, but feels that it would be a pity if it were not designed to include the existing A.S.T.M. D.285 in the range.

The authors' apparatus gives a certain cut at about 195° C., which would be obtained at about 183½° C. by A.S.T.M. D.285.

The flask designed by the speaker takes a charge of 1000 ml., a scale which is suitable for a producing company. This flask has been adopted in his laboratory for routine work, with satisfaction.

The speaker then offered a few criticisms on practical details.

Mr. HUGH SCOTT: The only thing I would like to bring in to support Mr. Richard's statement is that he did not wish to limit the amount of gasoline, but to make a standard test that should be capable of being correlated with the Bureau of Mines method. It is obviously, from a producing company's point of view, a waste of time to carry out detailed tests which are not to be correlated with the Bureau of Mines method.

For the purpose of correlating oils, an extremely important factor is the gas-oil content. If you are going to lose this to suit commercial ends, the test will be of no value from the point of view of geological correlations.

As far as I heard Mr. Richard, he did not wish to change the quantity so much, as to make it capable of correlation with the existing standard.

Mr. NEWTON commented on the temperature at which cracking develops, and said if several cuts were taken over 10° C. intervals, starting at 210° C. on Trinidad crude, it would be found that appreciable cracking commences from 230° to 240°. He did not think any conversion method could possibly give accurate consistent results if the temperature is allowed to exceed 260° C. for any length of time.

Mr. A. E. GERTY (written communication): With reference to Mr. Newton's remarks concerning the possibility of cracking taking place during the distillation, it should be pointed out that, in tests so far carried out by the method described, the successive gas-oil fractions drawn off have shown successively higher flash points. It might be mentioned here that this was the case where as much as 90 per cent. of the original crude-oil charge had been distilled off. A further point which should be noted is that the initial boiling points of the composite gas-oil distillates were generally higher than the final boiling points of the light fractions. In some few evaluations there was an overlap, but this never amounted to more than 10° C. Further, the flash points of the composite gas-oil fractions were never below 150° F. The above would appear to indicate that cracking, if such does take place, is so slight as to be negligible for all practical purposes.

It was also suggested by several members present that the allowable loss figure set by the authors was too high. This might possibly be true for the type of crude oil produced in Trinidad or in those cases where the producer operates a natural gasoline plant, and this in effect markets a more or less stabilized crude oil. Reports on properties of crude oils issued by the U.S. Bureau of Mines frequently show loss figures in excess of 2 per cent., and occasionally as high as 3 per cent.

In connection with the criticism of the condensing system, members seem to have lost sight of the fact that, in addition to the Liebig type condenser, two receivers arranged in series and cooled by immersion in an ice-water mixture are provided. The temperature of the water circulated through the condenser during distillation of light fractions could be kept lower with advantage.

To obviate the loss of butanes mentioned by Mr. Melvill would necessitate the provision of comparatively elaborate condensing equipment which would not be available in all laboratories, and, further, would not be justified in attaining the primary object of the evaluation method as stated by the authors. The loss figure in this connection would, however, provide a rough guide as to the amount of work likely to devolve on the absorption or other recovery system at the refinery.

Mr. PALMER replied: Mr. Berry and Mr. Melvill have both brought up the matter of the loss involved in the distillation. Mr. Berry suggested that we should use cooler water, and it is his opinion, I think, that we seem to be losing some of our light fractions. I might say that we consider 2 per cent. allowable loss might be a useful figure to standardize on. It is a fact that in our determinations with this method we have had a number of losses of the order of 0·1 and 0·2 per cent. Occasionally on very light crude we have had about 2 per cent., but I think that in general losses of the order of 1 per cent. are considered normal.

Regarding Mr. Richard's remarks, the apparatus we have outlined in this paper is probably not suitable for the requirements of a producing company, as Mr. Richard has stated. He has suggested several features in which he considers the apparatus could be improved, first, with possible use of different sizes of flasks. I can quite appreciate his point, but I think that if people used several different sizes of flasks, there would be endless arguments about the results obtained in particular tests. I cannot see otherwise than that there should be one standard form of apparatus.

Regarding Mr. Scott's remarks, I think the method very suitable for the purpose he referred to, because as we say in the paper, the choice of fractions is purely arbitrary, and you can run the test to any kind of fuel oil you like. Furthermore, you can concentrate on the gas oil and forget the fuel oil altogether.

In connection with a run to a certain cutting point, I think this should be ideal for correlation work. We run to fuel particularly, because of what we have to do with fuel oil.

With regard to Mr. Newton's comment regarding the temperature at which cracking develops, according to statements made by various authorities, cracking is considered to develop over a range of temperatures, but from all the evidence I have been able to find, 300° C. in the liquid is considered safe. We ran this apparatus to 300° in the liquid, and so far have not had any samples which showed signs of cracking.

Other standard methods carry distillation to appreciably higher temperatures, in which case cracking definitely does occur.

With regard to the various points which have been raised, I do want to stress this particularly, that the fundamental point in preparing the method was this: that existing standard methods do not give enough material to work with in the laboratory, and it is absolutely essential that sufficient material be obtained quickly in order that its quality may be studied.

In all our local refining practice we have a number of different crudes to work with. A number of them seem to change from time to time, and we must have a method which will give us important information concerning, in particular, octane number and the ignition quality of the gas oil.

The CHAIRMAN accorded a hearty vote of thanks to the authors for their paper, and to the Trinidad Leaseholds for the use of their Club Room.

PETROLEUM FUELS FOR SMALL-SCALE INDUSTRIES. *

By P. H. Herring (Member), and H. F. Jones, M.C. (Assoc. Member).

Synopsis.

This paper is confined to the use of petroleum fuels as applied to small-scale industrial uses.

The use of oil in internal-combustion engines as a source of power for small industrial uses is not treated in detail, as knowledge of such application is widespread.

A number of industrial applications of oil-firing are described as being typical of the wide range of purposes for which oil-fuels are used in various trades. These include examples of automatically-controlled firing.

The recent development of a complete portable oil-firing unit generating its own atomizing power is included, as this type of burner, with capacities varying from about 1 litre to 40 litres of oil per hour and ability to use a wide range of oil-fuels, is of considerable importance to small industries requiring a ready and simple means of applying intermittent firing.

The properties and some applications of liquid gases derived from petroleum are included.

Central heating of works, etc., is mentioned, and the development of automatic burners to use heavy oils is described, with reference to British Standard Specifications for Automatic Burners and for Fuel Oils.

In assembling material for this paper, difficulty arises in distinguishing between small-scale industries which use fuel oils and those applications which, whilst on a small scale, form a branch of a large industry. For instance, road-building is no small industry, but the heating of bitumen or tar boilers and the heating of road surfaces under repair are small but highly important sections of this industry. The authors have therefore included a number of such small-scale applications in illustrating the successful use of petroleum for industrial operations where the essential characteristics of the fuel are :

(1) Large heating value in small bulk.
(2) Convenience and safety under conditions of transport, handling and storage.
(3) Simplicity in application and control.
(4) Flexibility and ease of starting.

The generation of power by oil engines, because of its great importance in almost all industries, has become a matter of world-wide knowledge, and is therefore not enlarged upon in this paper. However, it is of interest to small industries that the modern engine, even in moderate sizes, consumes not more than 215 gm. of heavy petroleum fuel per H.P./hour, and that an extremely wide range of types, power output, speeds and weight are available from which to select the engine best suited to any particular requirement. Oil engines are widely applied in small industries to pur-

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poses which vary from driving the workshop machinery to distributing the finished product to the customer.

As a readily available source of heat, petroleum fuels have not only become firmly established in almost every industry, but their use is rapidly increasing. They are particularly important in small industries, owing to their ease and safety in storage and distribution within the works and the cheap and simple means which have been developed for their economic utilization.

The instances of the use of petroleum fuels which follow are far from being exhaustive; they are cited merely as representative examples and innumerable variations of those mentioned are in everyday use.

Metal Reducing Furnace.

This example consists of a small reverberatory furnace used for the reduction of tin, lead and antimony residues and oxides.

The raw material is charged into the furnace through an opening in the roof. The furnace is fired at one end with two air-jet burners. Secondary air for combustion is induced by chimney draught through ports situated underneath the burners, and the furnace atmosphere is controlled by dampers.

The furnace, being small, is not equipped with a recuperator. Firing is operated by the attendant who charges the furnace and runs off the metal. The fuel used is a heavy industrial furnace oil.

Figures indicating general running conditions are as follows :

Charge into furnace . .	5–7 metric tons, according to density.
Period of firing . .	8–12 hours, according to the material.
Rate of firing . . .	Approx. 0·9 kilos of oil per minute per burner.
Compressed air to burners .	Pressure up to 0·7 kilos per sq. cm.
Compressed air to burners .	Consumption, 1·4 cu. metre of free air per kilo of oil.
Approx. furnace temperature	1400° C.
Average ratio of oil-fuel burned to residue treated	1–5 by weight.

The same type of furnace is used for reducing swarf from precious metals such as silver, gold and platinum.

Bell Casting.

A small foundry using furnace oil for melting " bell metal " provides a somewhat similar application to the reducing furnace quoted above, but the operating temperature is lower. This furnace is used for varying weights of charge, say, between 2 and 6 metric tons. The short time taken to bring the metal to pouring temperature, the small quantity of fuel used and the easy control of the whole furnace operation have proved a source of gratification to the users, and the furnace was operated on intermittent firing for some years before repair was necessary.

Crucibles for Metal Melting.

One of the most convenient methods of obtaining small quantities of molten metal is that offered by the use of oil-fired crucibles. For small industries common arrangement consists of a crucible housed in a refractory-lined casing which is mounted on a frame. This frame also carries the oil-burning equipment. Crucibles of small size are arranged to lift out for pouring, but with larger sizes a more convenient assembly has both crucible and housing mounted on trunnions for tilting, thus permitting the metal to be poured without removing the crucible.

Crucible burners are usually operated by low-pressure air (fan blast), and various grades of furnace oils are suitable for firing the small combustion-chamber provided between crucible and the surrounding housing. Fig. 1 shows the general arrangement of an oil-fired crucible.

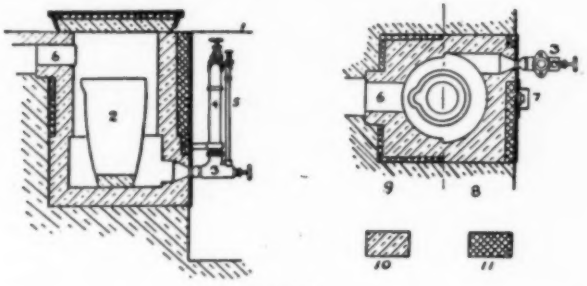

Fig. 1.

ARRANGEMENT OF LIFT-OUT OIL-FIRED METAL MELTING CRUCIBLE.

1 Floor-level.
2 Crucible.
3 Oil-burner.
4 Air-pipe.
5 Oil-pipe.
6 Flue.
7 Spilt-metal Run-out.
8 Half-section through Centre-line of Burner.
9 Half-section through Flue.
10 Firebrick.
11 Insulation.

Smith's Hearths.

A form of blacksmith's hearth using fuel oil provides a flat platform of firebrick at convenient height, with an aperture in the centre. Combustion is commenced in an enclosed space under the hearth, and the resulting flame rises through the opening. The material being heated can be enclosed by loose firebricks laid on the hearth to suit its size and shape, and burner controls are provided to regulate the characteristics of the flame. This form of heating is particularly clean, as no unburned fuel can make contact with the work, and flame regulation reduces scaling to a minimum. Furnaces of similar types are used for pipe-bending.

Muffle Furnaces.

Oil-fired muffle furnaces, with their use in many manufacturing processes, provide an excellent example of maintaining closely controlled temperatures. The burners and the flame travel are easily arranged to

produce evenly distributed heating over the whole surface of the muffle and, as uneven or intermittent firing is eliminated, with its attendant stresses and strains on the muffle, the life of the furnace is considerably prolonged and the quality of the work is maintained at a high standard. The use of small oil-fired muffle and semi-muffle furnaces for such purposes as tool hardening, annealing and other heat-treatment processes has been adopted in many works, and a somewhat larger application is the muffle furnace used for the vitreous enamelling of metal. Low-pressure air-burners are the usual means of oil-firing furnaces of this type.

Fritting Furnaces.

In the enamelled-ironware industry, preparation of "frit" for enamel requires careful attention to temperature and cleanliness of the firing. The furnace may be of the stationary built-up type, but the tendency is now to use a rotary type of furnace consisting of a metal drum coned at each end and lined with refractory material. An oil-flame is projected in at one end, and the hot gases emerge from the other. The drum is supported on bearings, so that it can be both rotated and tilted. The rotation effects economy in time and fuel during the heating process, which is carried out with the drum in a horizontal position. The provision for tilting the drum provides an easy means of expelling the charge. Oil-fuel, with its rapid heat generation, clean atmosphere and absence of ash or other constituents which would impair the quality of the frit, has proved an ideal fuel for this purpose.

Aluminium Melting.

Many small works are engaged in the production of aluminium castings, and a large proportion of these use oil-fuel in melting raw material for the preparation of various alloys. In such works the melting-pots are usually of 50 kilos and 150 kilos capacity, and the pots have in the past frequently been of metal construction, but there is now a tendency towards the use of graphitic pots. The practice in the smallest works is to use one pot for melting, and the molten material is dipped from this for pouring into the moulds. Cold ingots and scrap are added to the pot as required.

In works where more care is given to the preparation of correctly proportioned alloys, the melting-pot is used for blending and melting only, and the molten metal is afterwards transferred to maintenance-pots, where it is kept at the required temperature for pouring into the moulds. Low-pressure and medium-pressure air-burners form the usual method of firing both melting- and maintenance-pots and industrial petroleum fuels are used.

The following figures regarding fuel consumption may be considered as conservative :

50-kg. baling-out furnace on continuous melting	8 kilos of oil per 50 kilos of metal.
150-kg. baling-out furnace on continuous melting	6 kilos of oil per 50 kilos of metal.
50-kg. maintenance-pots . .	3·5 kilos of oil per hour.
150-kg. maintenance-pots . .	5 kilos of oil per hour.

Glass Works.

In the production of some of the higher qualities of glass, oil-fuels play an important part. Although oil is much used in large furnaces for the production of glass bottles and in annealing furnaces, the smaller type of works engaged in the production of fine grades of glass is referred to here. In these cases it is necessary to maintain the molten material in a particularly clean state, and free from vitreous masses which interfere with the drawing of the glass into its finished forms. From the large range of petroleum fuels which are commercially obtainable, such manufacturers are supplied with suitable oils to assist them in attaining the high quality demanded in their products.

Quarries.

Whilst a large proportion of quarries use oil-engines for driving air-compressors, stone-crushers, conveyors, and grading screens, etc., oil-firing is also used in this industry for such purposes as the preparation of road-dressings which consist of stone carefully graded to size and covered with a bituminous coating.

The stone is dried and heated by passing through a cylindrical rotating kiln set at an angle to the horizontal. An oil-burner is fixed at the lower or outlet end of the kiln, and the stone is fed in at the other. Before emerging from the kiln, all moisture has been eliminated, and the stone reaches the required temperature to facilitate the deposition of the bitumen thinly and evenly over its entire surface.

On leaving the kiln a measured charge of hot stone falls into a rotary hopper, which already contains the prescribed quantity of bitumen. Rotation of the hopper ensures a thorough mixing of stone and bitumen, after which the charge falls into the distributing vehicles or to the storage-bin.

A typical small-sized kiln of this type would be about 1·2 metres diameter, 6–9 metres in length, and the oil-burner would have a capacity up to approximately 18 litres per hour. The oil-burners are usually either the low-pressure air type, using air at about 25 cm. water gauge, or of the medium-pressure air type, using air at from 0·2 to 0·35 kilo per sq. cm. The exhaust fumes from the kiln are carried off by means of a chimney.

A somewhat novel use of oil in quarrying is for breaking down large masses of slate. Experiments have been conducted in which an oil-flame is projected on to the working face of the quarry. After a period of heating the slate disintegrates into pieces of convenient size for subsequent operations.

Bitumen Heaters.

Oil-fuel has proved an ideal means of firing plant of this description. The heaters are frequently fitted with spraying pump and nozzles, and a small petrol- or paraffin-driven engine is mounted on the unit to drive the spraying pump. A small rotary air-compressor with clutch is mounted near the engine, and this provides a medium-pressure air supply for the oil-burner. When the bitumen reaches the required temperature, the burner is shut off, the compressor clutch is thrown to the idle position, and the engine then pumps the contents of the heater through the sprayers

on to the road surface. The easy control of the oil-flame and the fact that it can be cut off immediately the desired temperature is attained minimize risk of the contents of the heater boiling over.

In the case of heaters not fitted with spraying gear, the cost of an engine may be saved by using portable self-generative burners, as these operate independently of any external power supply. A burner of 12-litres-per-hour capacity is fitted to a 1000-litre bitumen heater and the heating period is about 1½ hours.

Road Heaters and Driers.

For repairing the surfaces of bitumenized road carpets, the necessity arises to dry and heat the top layer, which is frequently saturated with bitumen squeezed up from the lower layers.

The heater consists of an inverted hood or cowl mounted on a truck, so that its opening is just clear of the road level. An oil-burner is fitted to generate flame under the cowl, and the heat is projected on to the surface of the road. The truck slowly travels over the road either by manual or motive power, according to its size, leaving the surface ready for immediate treatment.

Sizes of cowls in practical use are 1·2 metres square and 1·8 metres square, thus permitting treatment of appreciable road areas at one travel.

Bread-Baking and Confectionery.

In this industry oil-firing is applied to steam-tube ovens, side-flue ovens, hot-air ovens, etc.—in fact, to almost every kind of oven used in the baking of bread and pastry.

In some areas the side-flue oven is much used in small bakeries. These vary from about 2·7 metres to 3·3 metres square, the latter being rated as a "two-sack" oven. An example of practical operating conditions on an oven of this type is as follows:

The oven is fitted with a medium-pressure air-burner of 18-litres-per-hour capacity. Starting from cold, the firing continues for 1 hour to bring the oven to baking temperature. The burner is then shut off and the oven charged with 190–200 loaves, each weighing approximately 0·9 kg. When these are baked and withdrawn, the oven is fired for a further 10 minutes, followed by a similar baking operation. A second baking charge is then immediately put into the oven, and this second charge may be similar to the first, or may consist of smaller pieces—such as rolls—depending on the heat-retaining qualities of the oven. From this point firing periods of 10 minutes are followed by double batches of baking throughout the working period.

Baking ovens are commonly fired with either medium- or low-pressure air-burners or rotary burners.

In an example of a continuously-fired oven producing a high-quality cereal food, the products of combustion pass direct from the firing-chamber into the oven, and are in contact with the food. This is also the case in many other ovens, such as those producing ship's biscuits, bread for sausages, etc., and this practice provides an excellent tribute to the cleanliness of combustion obtained with oil-firing.

Further examples of oil-firing in the confectionery and catering industries are:

Frying-stoves for fish and chip bars.
Jam-boilers.
Sugar- and glucose-boilers.

Paint and Lacquer Drying Ovens.

There are many examples of oil-fired "stoving"-ovens, and the operating practice varies slightly in different applications.

A small oven engaged in the lacquering of tin-plate is heated by high-pressure sealed steam tubes similar to those used in some bread-baking ovens. One end of each tube projects into a small oil-fired furnace, and the remaining length of the tubes is distributed over the floor of the drying-chamber.

The hot exhaust gases from the furnace are also led through cast-iron pipes along the furnace floor to the stack, thus assisting in maintaining the desired temperature in the stoving-oven.

Other types of stoving-ovens are equipped with oil-fired air heaters, and the hot air is circulated by fans through the oven.

Yet another method is practised in which the hot gases from an oil-fired furnace are diluted with air and passed through the oven.

The system of heat transfer selected for work of this description is decided by the requirements of the manufacturer, but the essential in each case is economical heating and dependable control of the operating temperature, and for this reason oil-firing is largely applied to ovens of this type.

In the case of small stoving-ovens working on batch production, a considerable drop of temperature occurs as a hot finished batch is replaced by a cold one. The wide range of control available with oil-fired furnaces ensures a quick return to the required temperature. The usual practice is to use burners of the low-pressure or medium-pressure air types.

Bacon Factories.

The singeing of pig carcasses is conveniently accomplished with oil-firing. A vertical cylinder split axially into two sections forms the singeing-chamber, and this is mounted on a frame to permit one section to be easily swung away from the other. The carcass, which is suspended from a runway carried over the top of the singeing-chamber, is placed in position, and the singeing-chamber is then closed around it.

Oil-burners at the base are arranged to ensure that the flames sweep the interior walls, and thus perform the singeing operation.

Most bacon-factories are equipped with steam, and the burners are therefore usually of the steam-jet type. The petroleum fuel burned for this purpose is generally one of the lighter oils, such as gas oil or diesel oil.

As an oil-fired singeing-furnace is ready for use straight from the cold condition, the advantages it offers in regard to time and fuel economies are important, especially to the small factory handling a limited number of carcasses.

Printing.

The preparation of the carrying mediums used for printers' inks involves the necessity of closely controlled temperatures and careful precautions against fire. An example providing a combination of efficiency and safety is afforded by an installation fitted with an automatic oil-burner firing a small boiler which is charged with a high-boiling-point oil.

The thermostatic controls of the automatic burner ensure that the contents of the boiler are maintained very closely to the predetermined temperature. The oil in the boiler, which is merely a medium for heat transfer, is circulated to a number of jacketed pans, and thence back to the boiler for reheating, and is contained in a closed system.

The jacketed pans contain the oils which are heated in the preparation of the printing inks, and these are housed separately, and away from the boiler-room, thus eliminating risk of igniting vapour from the pans by the flame under the boiler.

Another application of oil-firing in the printing trade is the heating and maintenance of type-metal pots. For type-casting, close temperature control under varying load conditions is essential, and this is achieved by firing with an automatic oil-burner, which is controlled by a thermostat situated in the molten metal. This method provides a rapid heating-up from cold, a quick response to heavy demands on the pot for hot metal, and ensures against overheating the molten metal after its temperature has been raised to the working condition.

Readings taken on stereotype-metal melting- and maintenance-pots show the following fuel consumptions :

	7½-ton Pot.		3-ton Pot.	
	Melting.	Maintenance.	Melting.	Maintenance.
Duration of test . . .	7 days (168 hours)	7 days (168 hours)	7 days	7 days
Weight of plates cast . .	116 m. tons	—	45·7 m. tons	—
Amount of oil used in one week.	843 litres	398 litres	668 litres	272 litres

The automatic firing equipment installed on the pots referred to in these records is a pressure-jet oil-burner, such as is frequently applied to ordinary central heating and hot-water-supply boilers, and the usual controls, with electric spark for igniting the flame and safety devices against flame or ignition failure, are included. The chief variation from the usual central-heating equipment is that the controlling thermostat is constructed for operation at higher temperatures.

The diagram shows the arrangement of the pot furnace (Fig. 2).

Work on adapting automatic oil-firing to this particular purpose was commenced about 1930, and in recent years a number of such installations have been put into operation.

This example is a typical application of automatically controlled oil-firing to industrial purposes, where small quantities of heat, under more

accurate and cheaper control than can be provided by manual operation, are required.

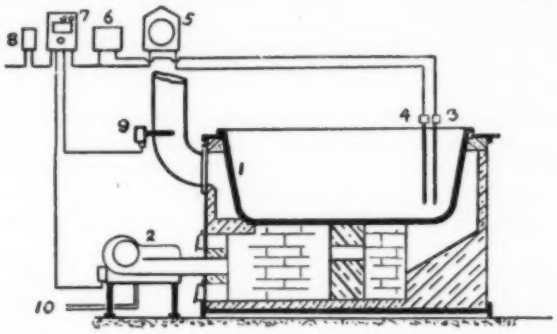

FIG. 2.

ARRANGEMENT OF AUTOMATICALLY OIL-FIRED TYPE-METAL MELTING-POT.

1 Melting-pot.
2 Automatic Oil-burner.
3 Thermostat.
4 Pyrometer.
5 Temperature Recorder.
6 Temperature Regulator.
7 Burner Control Box.
8 Main Switch.
9 Safety Control Flame-stat.
10 Oil Feed-pipe from Storage Tank.

PORTABLE SELF-CONTAINED OIL-BURNERS.

It will be observed that in most of the examples cited above the burners have been of types which require power for operation. For instance, the medium-pressure and low-pressure air-atomizing burners require a power-driven compressor or fan to supply the atomizing agent, the steam-jet burner depends on a source of steam supply and the automatic pressure-jet burner depends on a power-driven pump and an electrical circuit for the thermostatic controls.

Whilst the power required is very small, and in many cases only a small fraction of 1 horse-power is utilized, heating operations are frequently required where no power supply is available and a special power installation would be impracticable.

To cope with such conditions, much work has been expended on the production of self-contained burners which can operate independently of any external source of power.

Burners which vaporize petroleum spirits or light distillates, under pressure, have been used for many years where a limited amount of heat is required. Plumbers' blow-lamps, soldering-iron heaters and some varieties of cooking-stoves are instances of such burners. These burners are easily portable as self-contained units, but are very limited both in capacity and choice of fuel, and there has been a large gap between the pressure-vaporizer burners and the power-operated atomizing burners using heavy fuel oils.

This gap has been bridged by burners which generate steam to atomize their fuel. The name of " Self-Generative Burner " has been applied to a construction which embodies water-tank, oil-tank, flash-boiler, regulating

and safety devices, steam-jet, oil-burner and flame-tube all in one portable unit.

A burner of this type can be operated on a variety of petroleum fuels from distillates to light industrial fuel oils and the burning capacities range from about 1 litre to 25 litres of oil per hour, according to the size of the unit. In some of the larger models firing capacities up to 45 litres per hour are claimed.

For starting up, an air-pressure is raised in the water-tank by means of a foot-pump such as is used for automobile tyres, and the space in the tank above the water forms an air reservoir. Air from the top of the water-tank is used to atomize the oil-fuel, and the flame is ignited by a small torch. Pumping air into the tank must be continued until the oil-flame has heated

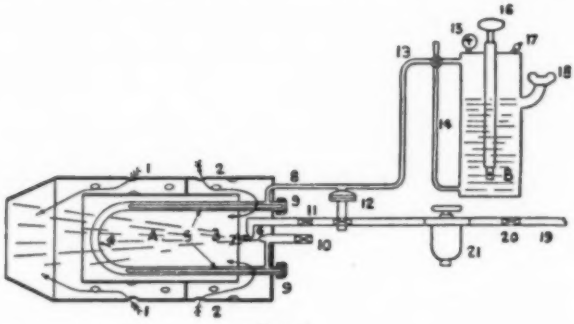

FIG. 3.

TO ILLUSTRATE PRINCIPLE OF SELF-GENERATIVE OIL-BURNER.

A. Burner.

1 Secondary Air Intake.
2 Primary Air Intake.
3 Flame Tube.
4 Boiler Tubes.
5 Boiler Core-rods.
6 Steam Jet.
7 Oil Jet.
8 Water Inlet.
9 Boiler Cleaning-plugs.
10 Steam-jet Filter and Cleaning-valve.
11 Oil-Metering Valve.
12 Automatic Oil Cut-off.

B. Water Tank.

13 Three-way Starting Valve.
14 Water Pipe.
15 Pressure Gauge.
16 Air Pump.
17 Pressure-regulating Valve.
18 Filler Cap.
19 Pipe from Oil Tank.
20 Oil Shut-off Valve.
21 Oil Filter.

the flash-boiler; the period required for this is only a few minutes. By means of a change-over valve, water is admitted to the flash-boiler, and the air is cut off from the burner. The air which is now sealed in the water-tank forces the water into the flash-boiler and no further pumping is necessary, as steam from the boiler atomizes the oil-fuel, and the burner will continue operation until oil or water is exhausted. A safety device is incorporated in the form of a diaphragm-valve which cuts off the oil in event of the steam-pressure failing. A blow-down valve, which is opened when shutting down the burner, is provided with the object of blowing out any solids deposited by the evaporated water. Oil and steam filters protect the burner nozzles from choking.

The burner nozzle is of the inverted scent-spray type, and the pro-

portion of water to oil used in firing is less than 1 to 8. The steam tubes are arranged for easy removal or renewal.

The accompanying diagram illustrates a form of self-generative burner (Fig. 3).

This type of burner has been described at some length as, owing to its portability, wide possibilities of application, and successful operation with light fuel oils, it is of considerable interest to the small-scale industrialist. It is especially applicable to conditions where moderate rates of heating are required over comparatively short periods and where the provision of power-operated burners presents difficulty.

Liquid Gases.

Two grades of liquid gas derived from petroleum are marketed for small industrial purposes. These are highly volatile products compressed to the liquid condition, and are distributed in steel cylinders of approximately 9·5 and 19 kilos capacity, and also in steel bottles of 10·5 kilos, the last being equivalent to approximately 5·7 cubic metres of free gas. The tare of the bottle is 16 kilos, and it measures approximately 30 cm. diameter and 57 cm. high. These gases are propane and butane, and they have the following properties :

	Vapour Pressure at 15·5° C.	Calorific Value.		Volume of free Gas per Kilo at 60° F.
		Cals. per Kilo.	Cals. per Metre³.	
Propane .	9·8 kilos per cm.²	11,900	22,000	0·54 metre³
Butane .	1·4 kilos per cm.²	11,700	28,600	0·41 metre³

Industrial applications of these gases include the following :

Propane.

The flame temperature of the oxy-propane flame is about 2500° C., and this is not high enough for welding steel, but the flame is successfully used in welding cast iron. It is also used for welding most non-ferrous metals, including aluminium and magnesium alloys, and for such purposes as lead-burning. It is particularly adapted for the welding of thin plates.

The use of the oxy-propane flame for cutting steel and scrap metal provides the advantages of smooth cuts with sharp edges and easily removed slag, and it is used with either hand or machine cutters.

Steel plates up to 40 cm. thick have been successfully cut with this gas.

It is also used in preparing surfaces against corrosion by metal-spraying and in building-up worn surfaces of running machinery.

Butane.

Where other sources of heat and light are unavailable, this gas is used for such purposes as portable lighting and small-scale heating. Typical examples of its use are provided by military and construction camps, mobile catering-stalls and hotels in remote districts. Such industrial

applications as soldering, degreasing plant, tinsmiths' work, paint-burning, and general work of this nature as may be encountered in garages, etc., are conveniently catered for by this fuel.

These liquid gases also provide a convenient means of controlling the atmosphere of small muffle furnaces and similar heat-treatment apparatus where highly accurate conditions are necessary.

Works Heating.

Automatic oil-burners are used for heating works, cinemas, hotels, etc., and also in conjunction with air-conditioning plants.

In England, burner development has been directed to the use of heavier and cheaper fuel oils than those which have, in the past, been regarded as "Domestic Fuels." A tax of 1*d*. per Imperial gallon imposed on imported fuel oils in 1933 has accelerated this development, and all the leading makers in this country now market burners equipped to use the heavier oils.

The chief modification to the burner designed for using heavy oil consists of a thermostatically controlled electric heater which maintains the oil-feed to the burner nozzle at the necessary temperature for efficient atomization. This is connected to the burner controls, so that the burner does not start until the desired oil temperature is attained. A safety device to prevent overheating of the fuel is an important feature of electrical preheaters.

An additional oil preheater using heat from the installation being fired, such as from a hot-water circuit, is frequently installed with the object of minimizing the current consumption of the electric heater.

The British Standards Institution of 28, Victoria Street, London, S.W. 1, has recently issued a specification (No. 799) for "Fully Automatic Oil-burning Equipment for Central Heating and Hot-water Supply," which indicates the practice generally accepted in England for the manufacture and installation of this type of plant.

British Standard Specification for Fuel Oils for Burners (Petroleum and Shale Oils) No. 742, 1937, provides three tables, specifying oils for Domestic Oil-burning Installations, Marine Oil-burning Installations and Industrial Oil-burning Installations, together with methods of testing oil-fuels.

PETROLEUM FUELS IN RELATION TO AGRICULTURE IN GREAT BRITAIN.*

By C. L. Gilbert, B.Sc., A.R.C.S. (Member), D. H. Meijnen, and K. H. Sambrook, B.Sc.(Tech.), A.M.I.Mech.E.

Synopsis.

The rapid growth in mechanization of British agriculture has resulted in a large increase in the consumption of petroleum fuels by agricultural tractors, stationary engines and transport vehicles.

The advantages of tractors over horses are discussed, and figures quoted showing relative costs of operation. Reference is made to the improvement in the efficiency and adaptability of tractors.

The present trends in the respective importance of gasoline, kerosine and diesel engines for agricultural purposes are indicated and supported by consumption statistics. Attention is directed to the effect of taxation on the relative consumption of these fuels.

The recent introduction to agriculture of new appliances and processes has created an additional demand for petroleum fuels.

The employment of oil-fired dryers for grass, grain, seeds and hops is described. In dairy-farming the premium obtainable for milk produced under approved conditions offers large outlets for oil-fired sterilizing equipment. The use of kerosine refrigerators is stimulated by the introduction of thermostatically controlled burners.

Kerosine burners are widely used in poultry-farming for incubators and brooders, and reference is made to large brooders heated with automatic fuel-oil burners.

The use of oil-heaters for frost protection in orchards is now well established, and continues to increase.

The consumption of petroleum oils for domestic purposes on farms, although affected by the increasing availability of public electricity supply, is still of the first importance, and attention is directed to recent technical improvements in oil-burning appliances for heating, cooking, hot-water supply and lighting.

Introduction.

In spite of the decline in the area of land under cultivation in Great Britain, the estimated consumption of petroleum fuels in agriculture has increased from 125,410,000 Imp. gallons † in 1932 to 174,800,000 Imp. gallons in 1937, an increase of some 40 per cent. This increase is, of course, largely due to the extended adoption of the internal-combustion engine for agricultural transport vehicles, farm tractors and stationary engines, and reflects the rapid growth of mechanization in British agriculture.

The introduction of new processes utilizing heat as well as power has created an additional demand for petroleum fuels which, although at present relatively small, shows signs of increasing rapidly.

The overwhelming advantage of petroleum fuels for power production through the medium of the internal-combustion engine has no parallel

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† The unit of volume used throughout this paper is the Imperial gallon (equivalent to 4·546 litres).

in the field of heat production. Nevertheless, oil fuels possess important advantages for this purpose, which have led to their choice for a number of these new agricultural processes, as will be shown by the examples given in this paper.

Finally reference must be made to the consumption of petroleum oils on the farm for lighting, heating and cooking, which, in spite of the increasing penetration of electricity supply in agricultural districts, is still of the greatest importance in respect both to the offtake involved and to the service rendered to the farmer. Outstanding technical advances have been made recently in the design and construction of oil lamps and heaters and in their adaptation to a wider range of appliances.

Power.

(a) *Tractors.*

The chief advantages to be gained by substituting tractors for horses are: first, lower operating costs, and secondly, the increased rate of working, which enables full advantage to be taken of favourable weather conditions, a factor particularly valuable in a variable climate such as that of Great Britain.

Whilst the operating costs per day for a tractor exceed those for a team consisting of a man and two horses, the amount of work done by the tractor is much greater in proportion to the daily costs. The following figures (Table I) are representative of the operating costs per acre when using horse-drawn implements and tractor-drawn implements respectively:—

Table I.

Operation Costs per Acre.

	Horse-drawn Implement.		Tractor-drawn Implement.	
	s. *d.*	*s.* *d.*	*s.* *d.*	*s.* *d.*
Ploughing	12 6 to	20 0	4 6 to	7 6
Cultivation *	2 6 „	4 0	2 3 „	2 9
Rolling	1 6 „	2 0	9 „	1 0
Harrowing	1 6 „	2 0	9 „	1 0
Drilling	3 0 „	5 0	1 2 „	1 6
Harvesting †	30 0 „	40 0	15 0 „	20 0

* Horses could not pull the deep cultivators that are used with tractors.

† The comparison is made between building, stooking, ricking and threshing and combine and drier.

Note.—The figures for tractor-drawn implements include an estimated average allowance for depreciation and repairs of tractor and implement of 2*s.* per hour.

Recent years have witnessed great improvements in the efficiency of tractors, the average fuel consumption of a kerosine tractor having been reduced since 1920 from 1·63 lb. to about 1 lb. of kerosine per drawbar horse-power hour. In the same period tractor weights have been reduced by nearly 40 per cent.

Concurrent with the improvement in general efficiency, great progress has been made in the production of types of tractors suitable for a variety

of purposes. Whereas formerly tractors were used mainly for heavy work in ploughing and harvesting, there are now few purposes for which they cannot be used in place of horses. The complete mechanization of the average farm requires about 10 horse-power of tractor power per 100 acres of arable land.

The choice between a large tractor and several small ones depends largely on the size and position of the farm, but the tendency is towards the use of a number of small tractors, since it is difficult to keep a large tractor permanently occupied, it being really necessary only for combine-harvesting.

A census taken by the Ministry of Agriculture in September 1937 showed that there were over 46,000 agricultural tractors in operation. The great majority of these are driven by gasoline/kerosine engines, but increasing use is being made of diesel tractors, particularly for powers exceeding 30 horse-power, in view of the lower fuel costs.

The present position in this respect is shown by the following figures (Table II), which also illustrate the enormous increase in the use of tractors during the last five years.

TABLE II.

Estimated Consumption of Kerosine and Diesel Oil by Agricultural Tractors in Great Britain.

	(Imperial gallons.)	
	1932.	1937.
Kerosine	20,000,000	40,000,000
Diesel oil	Negligible	1,000,000

Owing to the fact that gasoline has to pay the full tax of 8*d*. per gallon, the number and size of gasoline tractors are small, and the gasoline consumption for this purpose is relatively unimportant.

(b) *Stationary Engines.*

On the average farm, stationary engines are required to supply power for the preparation of feeding-stuffs, for water-pumping, driving hay elevators and milking machinery and for electricity generation where public supply is not available.

Table III shows the estimated consumption of gasoline, kerosine and diesel oil in stationary agricultural engines for the years 1932 and 1937.

TABLE III.

Estimated Consumption of Petroleum Products in Stationary Engines used in Agriculture.

	(Imperial gallons.)	
	1932.	1937.
Gasoline	300,000	500,000
Kerosine	12,000,000	20,000,000
Diesel oil	100,000	400,000

It will be seen that in the last five years the consumption of gasoline and kerosine has increased by approximately 66 per cent., whilst the consumption of diesel oil has shown a 400 per cent. increase. Kerosine engines account for over 95 per cent. of the total consumption. Moreover, the increased gasoline consumption is almost entirely due to the gasoline consumed in gasoline/kerosine engines during the warming-up period.

Except where a portable air-cooled engine is required, and for very small powers, the gasoline engine is now rarely used, owing to the high cost of the fuel, which has to bear the full tax of 8*d*. per gallon, whereas on kerosine and diesel oil used for stationary engines the tax is only 1*d*. per gallon.

The gasoline/kerosine engine is very popular with farmers, and seems likely to remain so, since it is cheap to buy and uses a comparatively cheap fuel. This type, however, requires care in operation, to ensure that the change over from gasoline to kerosine does not take place before the engine is sufficiently warm, and it is therefore more suitable for continuous than for intermittent work. The hot-bulb engine has the advantage of being simple and very robust, but, owing to its relatively low efficiency (low compression ratio) and the trouble involved in heating prior to starting, it is likely to be displaced to an increasing extent by the lighter, high-speed diesel engine.

(c) *Transport.*

The services rendered by motor transport in conveying agricultural produce to the market and railhead and in bringing raw materials, feeding-stuffs, and fertilizers to the farm are too well appreciated to require further emphasis. Improvements in motor vehicles have increased their adaptability, not only for road haulage, but also for internal purposes on the farm, whilst, conversely, the introduction of motor tractors fitted with giant pneumatic tyres has extended their use to road haulage.

The influence of the motor car on social life in farm districts is also worthy of mention.

During the quarter ending September 30, 1937, there were in circulation in Great Britain over 12,000 agricultural vans and lorries, excluding horse-drawn vehicles, of which all but eighteen were gasoline or diesel-oil vehicles.* The increase in the annual consumption of gasoline by agricultural vehicles and private cars used by farmers during the last five years is shown by the following estimates (Table IV).

TABLE IV.

Estimated Annual Consumption of Motor Spirit in Agricultural Vehicles.

	(Imperial gallons.)	
	1932.	1937.
Lorries	18,000,000	28,000,000
Private cars	35,000,000	54,000,000

* Ref. Ministry of Transport Census.

The use of motor vehicles in agriculture is encouraged by valuable concessions in both fuel and road taxes. For instance, kerosine, gas oil and fuel oil (imported or home products from imported crude) used in agricultural engines pay 1*d*. per Imp. gallon as tax in lieu of 8*d*. per Imp. gallon paid for use in other automotive vehicles.

Agricultural tractors which may have to be driven on the road in moving from one field to another pay a nominal annual tax of 5*s*. Tractors which are never driven on the road are exempt from tax.

The following examples illustrate the favourable rates payable by vehicles used for agricultural transport on the roads as compared with other commercial vehicles (Table V).

TABLE V.

Comparison between Road Taxes Payable by Agricultural and other Vehicles.

	Annual Road Tax.	
	Agricultural Use.	Other Use.
Gasoline lorry with pneumatic tyres with unladen weight between :		
1½ and 2 tons	£13	£25
3 and 4 tons	£18	£50
Tractor with pneumatic tyres, unladen weight 5 tons	£12	£90
Tractor with other tyres, unladen weight 5 tons	£12	£113 6*s*. 8*d*.

AGRICULTURAL DRYERS.

(a) *Grass Drying.*

The economic importance of grass drying lies in the possibility which it offers of dispensing to a large extent with imported food-stuffs for the maintenance of livestock in the winter months. These imports in 1937 amounted to over 6 million tons.*

In all grass dryers at present on the market the grass is dried in a current of hot air obtained by mixing the requisite quantity of cold air with the products of combustion of the fuel, a method particularly suited to the use of oil, owing to the ease with which clean combustion is maintained.

For the smaller plants, and particularly for portable or semi-portable plants, a light fuel oil of approximately 40 seconds Redwood I at 100° F. (1·8° Engler at 20° C.) is used. The larger fixed plants may be arranged to burn heavy fuel oil, providing that suitable arrangements are made for handling and preheating the heavier grades.

The consumption of oil-fired grass dryers at present averages about 80 Imp. gallons of oil per ton of dried grass, but the results vary widely, according to the air temperature employed and the moisture content of the grass fed to the dryer.

* 1 ton = 2240 lb.

(b) *Grain and Seed Drying.*

Certain types of grass dryers may be readily adapted for the drying of grain and seeds. The close regulation of temperature obtainable with oil fuel is an important advantage in dealing with these valuable products.

(c) *Hop Drying.*

In the South-Eastern counties and in the West of England the growing of hops is an important feature of agriculture. During the last six years a large number of hop-drying kilns have been converted to oil-firing, and in certain instances new kilns have been installed designed specifically for oil fuel.

Two types of kilns are employed, viz., direct-fired kilns and those fitted with so-called "pure-air" heaters. The latter type was introduced to avoid the danger of contaminating the hops with impurities, especially arsenic from solid fuels, but compared with the direct-fired kiln, it involves increased initial and maintenance costs and higher fuel consumption. Oil fuel, owing to its low arsenic content (less then 1 part in 2 million) and the clean combustion obtained, enables advantage to be taken of the simplicity and economy of the direct-fired system, whilst minimizing the risk of contamination.

In the earlier oil-fired kilns the oil was burned in a simple combustion chamber replacing the original solid fuel grate, but the modern tendency is to employ a specially designed furnace in which the products of combustion are mixed with the necessary diluting air and forced into the kiln under slight pressure by means of a fan. This permits a finer control of the temperature and deeper loading of the kiln, with more efficient utilization of the heated air.

A light fuel oil having a viscosity of approximately 40 seconds Redwood I at 100° F. (1·8° Engler at 20° C.) is employed in this application, the fuel consumption on direct-fired kilns averaging about 8 gals. per pocket (168 lb.) of dried hops.

Oil-firing has also been applied to a number of hop kilns fitted with "pure-air" heaters on the score of close temperature control and cleanliness. The fuel consumption is generally some 50 per cent. higher than that of the direct-fired kilns.

Hop drying is a seasonal operation, and the kilns are normally used for only two or three weeks in the year. There is, however, the possibility of employing them for drying other agricultural products, and, in fact, an oil-fired hop kiln has been successfully employed for grass drying.

Dairy Boilers.

A British dairy-farmer producing milk under conditions approved by the Milk Marketing Board is termed an "accredited" producer, and receives a premium of 1*d.* per gallon, which is paid by the Board from funds obtained by a general levy on all producers of milk.

An essential condition is the cleaning and sterilizing of all equipment after milking. For this purpose a small steam boiler is installed which

supplies hot water for washing the milk utensils and steam for a sterilizing cabinet and for sterilizing the milk machinery.

In the smaller dairy-farms dealing with, say, 30 cows, a boiler having an output of 60–70 lb. of steam per hour is required, whilst for larger dairy-farms a boiler producing about 120 lb. of steam per hour would be needed. The boilers are normally in operation for a period of 2–2½ hours twice per day.

The main advantages of oil-firing in this application are the ease and rapidity of lighting the boilers and of shutting down when sterilizing is finished without waste of fuel, and also the clean conditions obtainable around the boiler. This latter factor makes it practicable to install the boiler close to the sterilizing cabinet, thus economizing in space and facilitating supervision without detracting from the hygienic conditions in the dairy.

A number of oil-fired dairy boilers are already in successful operation, and the efforts now being made to develop more efficient boilers specially designed for oil-firing are expected to result in a rapid expansion in the use of oil fuel for this purpose.

The smaller boilers may be fired with simple burners of the vaporizing type, which have the advantage of requiring no power supply for their operation. These burners are supplied with an oil having a viscosity of approximately 35 seconds Redwood I at 100° F. (1·4° Engler at 20° C.). For the larger boilers atomizing burners are more suitable, which, although requiring power for their operation, can handle heavier and cheaper grades of oil. The oil consumption of the smaller dairy boiler averages about 1500 to 2000 gals. per annum.

Refrigerators.

A number of refrigerators, particularly among the smaller types, are heated by kerosine. Recently an important technical advance has been made in this application by the introduction of thermostatic control, in conjunction with wickless burners. This enables constant temperatures to be maintained in the refrigerator, whilst the type of burner employed will run for an indefinite period without attention.

Kerosine-heated refrigerators are very economical; for instance, a burner capable of heating any normal domestic refrigerator consumes only 0·0066 gal. (30 c.c.) of kerosine per hour when burning at full flame, the average consumption under thermostatic control being considerably less.

Incubators and Brooders.

Previously regarded as a minor sideline on general farms, poultry-farming is now an important agricultural industry, and it is estimated that the total output, by weight, in Great Britain of eggs and table poultry now exceeds that of cereals. The use of incubators and brooders for the hatching and rearing of chickens enables full advantage to be taken of seasonal demands and variations in price. The majority of small incubators employ simple kerosine lamps, which have the advantages of ease of control, cheapness and reliability. Modern types are fitted with a thermostatic device

which maintains the incubator temperature at the required value. A typical burner has a consumption of 0·01 gal. (45 c.c.) of kerosine per hour, and is capable of heating an incubator holding up to 250 eggs.

Kerosine-heated brooders are widely used for chicken-rearing, as they are cheap, economical to operate and easily handled and regulated. A burner of the same capacity of that mentioned above is capable of heating a brooder accommodating 100–150 chickens.

A type of oil-heated brooder now being employed by some of the larger producers consists of a large building containing a battery of unit brooders, each comprising a number of trays arranged in tiers. Warm air from a central air-heater is distributed to each tray and a proportion of the air is recirculated.

The air-heater is fired by a fully automatic burner controlled by the temperature of the air delivered to the brooders.

The operating cost of an oil-fired brooder of this type having a capacity of 25,000 chicks is stated to be approximately £10 for the period of three weeks during which the chicks remain in the brooder, or rather less than one-tenth of one penny per chick.

Orchard Heating.

Within the last six years increasing interest has been shown by fruit-farmers in the possibility of protecting their trees from the effects of unseasonable late frosts by employing a number of oil-heaters distributed throughout the orchard. The success of this method of heating depends on the fact that during a frost, which almost invariably occurs in calm weather, the temperature of the air close to the ground is several degrees lower than that of the air 10–15 ft. above ground-level. If the air close to the ground-level is heated, it rises until it reaches a layer where the surrounding air is at the same temperature, when further upward movement is arrested. Thus, a gradual warming of the air in the orchard takes place from above downwards, and the volume of air to be heated is limited to a comparatively shallow layer.

The oil-heaters, of which about fifty or sixty are required per acre, are of very simple construction, and cost in the neighbourhood of 3*s*. each. Fuel is burned, the consumption being one-third of a gallon per hour, so that the average consumption per acre is roughly from 15 to 20 gals. per hour. Statistics indicate that, on the average, about two nights of late frost may be expected per annum, each necessitating the lighting of the heaters for about 4–5 hours.

This method of protection against frost has recently been extended successfully to soft fruits and early vegetables. The total number of heaters installed at the end of the 1937 heating season was estimated at 37,000, and continues to increase.

Domestic Uses.

Whilst the increasing availability of public electricity supply naturally affects the consumption of kerosine for domestic purposes, this factor is likely to be counterbalanced in the future by the remarkable improvements

which have been made in recent years in the design of kerosine-burning appliances.

(a) *Heating.*

The older types of cylindrical chimney stoves are now being replaced by heaters in modern design and attractive appearance which are not only completely odourless, but in some instances provide radiant heat as well as convected warmth. These modern kerosine heaters have the advantage of portability, and are strictly competitive, as regards initial and operating costs, with other forms of heating. Hot-water radiators of both fixed and portable types heated by kerosine burners are also on the market.

(b) *Cooking.*

There has been considerable development in the design of cooking appliances, notably in the introduction of blue-flame and wickless burners. The availability of kerosine cookers of modern design and appearance, from single burners to large ranges complete with ovens, is expected to increase the demands for this type of equipment.

(c) *Hot-Water Supply.*

A further possibility for the increased consumption of kerosine in farmhouses is offered by the introduction to this country of thermostatically controlled water-heaters fitted with kerosine burners. If required, the burners may be supplied from fuel storage outside the house, so that there is no necessity to handle the kerosine. These heaters can compete favourably with other forms of energy giving rapid and controlled heating.

(d) *Lighting.*

Although this application of petroleum fuels is the most likely to suffer from the increased availability of electricity on farms, gasoline and kerosine lamps will continue to be widely used, not only where electricity is unobtainable, but also for temporary lighting, portable lamps and in scattered outbuildings. Improvements continue to be made in gasoline and kerosine lamps, among which may be mentioned the incandescent-mantle lamp heated by wickless burners or burners of the pressure type.

OBITUARY.

David Holde.

By the death of Professor Dr. D. Holde, who died aged 74 in Berlin on 4th June, 1938, the science of mineral oils, fats and waxes has lost one of its most prominent representatives. Holde was known to the oil chemists throughout the world for his numerous scientific papers, but above all as the author of the famous book "Kohlenwasserstoffoele und Fette" (Hydrocarbon Oils and Fats), the latest (seventh) German edition of which was published in September 1933, a few months before the author's seventieth birthday. Soon after the publication of that edition, the life honorary membership of the Institute of Petroleum was conferred on him.

Holde was born on the 1st February, 1864, at the small town of Crossen on the Oder (Prussia). In 1883, soon after leaving school, he took up the study of chemistry at the Berlin University, where he was among the pupils of A. W. von Hofmann. Having spent one term at Heidelberg working under Bunsen and attending the lectures of Quincke, he returned to Berlin for the work on his doctor's thesis under F. Ruedorff. In the summer of 1887 he took his doctor's degree in Berlin with a thesis on the solubility of sulphates in sulphuric acid, a rather dull subject, but carried out with all the accuracy for which his later investigations were outstanding.

Only a few weeks after passing his examination, at the age of twenty-three, he found his first position at the Royal "Mechanisch-Technische Versuchsanstalt" of Charlottenburg (later the "Material-Pruefungs-Amt" of Berlin-Lichterfelde, the official German Institution for Testing Materials), where he was to stay for the whole of his career. The first problem for the investigation of which he was employed was decisive for all his further professional activities. It was the question whether the then newly introduced mineral lubricating oils were equivalent to the colza-oil or rape-seed oil which up to then had been almost exclusively used for lubricating purposes.

At those times, however, there were scarcely any methods known for testing lubricating oils. Consequently, Holde's work had to start with developing methods of oil analysis, and that was the work in which he was to be engaged for many years to come and which was to be the foundation-stone of his world-wide renown.

After three years' work at the Versuchsanstalt, he was appointed head of the newly created Oil Department of that institution. That position, the importance of which increased with the further development of oil analysis, largely due to Holde's own efforts, he kept until 1917, when he resigned on account of bad health.

In 1897, after ten years' work on the development of methods of oil analysis, Holde published the first edition of his book, then a small volume of 259 pages called "Untersuchung der Schmiermittel" (Examination of Lubricants), and being to a large extent a summary of the papers published in the previous years by Holde and his collaborators. Six further editions of the book followed in the course of thirty-six years, each of them almost entirely re-written and enlarged, the last one containing more than 1000 pages. The continual extension of the scope of the book was indicated by the changes which its title underwent: from "Examination of Lubricants"

to "Examination of Mineral Oils and Fats", "Examination of Hydrocarbon Oils and Fats" at last to "Hydrocarbon Oils and Fats," showing that the last editions were dealing not only with the analysis, but also with the chemistry, physical properties and technology of various kinds of oils. Several of the later editions were translated into English and French.

Apart from this book of his own, Holde contributed large sections to the standard works "Das Erdoel" by Engler-Hoefer, "Chemisch-Technische Untersuchungsmethoden" by Lunge-Berl, and "Handbuch der Chemie und Technologie der Oele und Fette" by Ubbelohde-Goldschmidt.

Naturally, neither the writing of the books nor the underlying experimental work could be done entirely by Holde himself, but he always knew where to find able and devoted collaborators, several of whom have gained a high reputation of their own, such as Dr. W. Normann, the inventor of the technical hydrogenation of fatty oils, Prof. Dr. L. Ubbelohde, Prof. Dr. J. Marcusson, and others.

Holde's scientific investigations carried out at his High-School laboratory as well as at the Material-Pruefungs-Amt, apart from the routine testing work, covered a wide variety of subjects, the common denominator of which, however, was their relation, in one way or other, to oils, fats, waxes or their derivatives. An object of special interest to him was the composition of the natural mixed glycerides and of the saturated fatty acids, in particular the question whether or not these acids possessed exclusively straight chains and even numbers of carbon atoms. Other favourite subjects of his were the constitution of lubricating greases, the electric excitability of naphtha, the coefficient of expansion and the viscosity of mineral oils, the hydrolysis of aqueous and alcoholic soap solutions, the preparation of the anhydrides of the higher fatty acids and their utilization—*e.g.*, as edible fat substitutes. The number of scientific papers published by Holde either by himself or jointly with his collaborators far exceeds one hundred. A thorough study of his papers reveals the fact that the basic ideas, and sometimes even the particulars, of more than one apparently new discovery had been found and described by Holde many years ago.

The part he played in the oil world was shown by his active and often leading membership of important bodies concerned with the science and analysis of oil, such as the International Petroleum Committee, the lubricants section of the D.V.M. (German Society for Testing Materials), the "Wizoeff" (the German central organization of scientific oil and fat research, which published the German Standard Methods of Fat Analysis), and others. As a German delegate he took part in several International Congresses.

His life's work is for ever recorded in the annals of science; his noble and benevolent personality will never be forgotten by his many old friends and pupils.

W. B. AND F. F.

THE MANUFACTURE OF CUTTING OILS.*

By John F. Miller.†

Cutting oils are highly specialized products, and their manufacture calls for a very sympathetic interpretation of the known requirements of such media. In the evolution of suitable formulæ, the experimental work of the research chemist and metallurgist has to be aligned with the service requirements of the production engineer, and these totally different factors must then be merged so that the machine-tool maker has no grounds for criticism.

Through the years, cutting oils have seen many changes. It is generally agreed that plain water was the first medium used to offset the generation of frictional heat in metal-cutting. It was soon evident that, despite the attractions of negligible cost and ready supplies, there were other considerations which militated against its use. The heavy rusting it caused was a profound disadvantage not appreciably lessened by the addition of soda. Although water is still the finest coolant as such, it was found that metal-cutting also demanded a certain degree of lubrication from the medium in use. And so the soft-soap solutions came into being. They were prepared by dissolving soda in water and adding lard oil, the free fatty-acid content of which combined with the soda to give a soap solution, which in turn emulsified the neutral oil. The finished product was rather unstable, yet gave fair service in the less exacting machine-shop conditions of the period.

The cutting media already mentioned were all water-base auxiliaries to the firmly established fixed oils which have not been entirely supplanted right up to the present day. Oils such as rape, sperm and lard have rendered a unique service to engineers for many decades, and although still preferred by some for lubricating heavy-duty broaching, tapping and screwing operations, they are now obsolete on the high-production machine tools where the heat generated is sufficient to break them down.

Cutting Pastes.

Reverting to the emulsifiable oils, cutting pastes represented the next step forward—and a notable step it was, for the cutting paste was probably the first coolant product to be offered to engineers by an outside manufacturer, previous materials having been prepared in the engineers' stores. These pastes owed much of their undoubted efficiency to the shaping influence of war-time production. Although they needed a certain amount of patience in mixing, they possessed excellent adherence to the metal

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† Messrs. Fletcher Miller, Ltd.

being machined, a factor which explains their use in certain shops to-day. Cutting paste was manufactured from a formula reading:

Lubricating oil	150 parts
Oleine	85 parts
Caustic soda	6 parts
Water	250 parts

Its success opened up possibilities for extending the use of aqueous emulsions, and by adapting knowledge gained in the leather and textile industries, the so-called soluble oil was evolved.

Soluble Oils.

Soluble oils vary greatly in their composition, method of manufacture and emulsifying powers. It may be relevant here to quote what some typical soluble oils contain. A moderately useful oil is prepared by mixing 1 part of rosin oil with 10 parts of lubricating oil and adding 20 per cent. caustic soda solution until a clear oil results which emulsifies with water. Another formula reads:

Lubricating oil	250 parts
Rosin	22 parts
Oleine	22 parts
Caustic soda	3 parts
Water	10 parts

and industrial alcohol for thinning back.

Some soluble oils are little better than disinfectant fluids, and are prepared commercially by sulphonating castor oil, adding lubricating oil and cresols. The true sulphonated type of emulsifiable oil is the most frequently used to-day, and this is because it is so adaptable to different machining operations. Here is a typical formula:

Sulphonated soya-bean oil	13½ parts
Sulphonated castor oil	25 parts
Lubricating oil	17 parts
Water	32 parts

and sufficient caustic soda 20 per cent. solution to give an oil of bright appearance.

Soluble oils are also made from the by-products of white-oil manufacture—I refer to what are generally termed naphthenic acids, which, when mixed with mineral oil, rosin and caustic soda, yield a product giving a milky-white emulsion with water. A totally different type of soluble oil is also prepared from naphthenic acids, and these are known as the clear or translucent soluble oils, which form a finely dispersed emulsion with water and possess a fair degree of clarity.

Straight and Compounded Oils.

The neat or straight oils are not emulsifiable with water, and are employed direct from the barrel or after dilution with light-bodied mineral oil. In the early days of machining the only representatives of this type were the

fixed oils, such as sperm, lard or rape. Whilst they have never been obsoleted entirely, their place has been largely taken by the compounded oils. Straight mineral oils have been moderately useful for machining, but current practice makes use of various addition agents such as oleine, lard oil and sulphur to improve the finished product. Sulphurized oils are much used, and are usually a blend of mineral and fatty oils with which powdered sulphur is permanently introduced during manufacture. A heavy-bodied concentrate is produced, and is regarded as a base oil which is normally thinned back with further mineral oil before use. A typical formula for sulphurized base oil is:

Lard oil	50 parts
Mineral oil	50 parts
Wool Grease	10 parts
Sulphur	8 parts

The inclusion of wool grease is optional.

Variations of this class of oil are the pale, sulphurized media which are relatively pellucid and are employed when it is desirable to have a clear view of the tooling in progress. Also one must mention the so-called automatic oils, which are prepared to suit the machining conditions on automatic and semi-automatic lathes. The presence of even 5 per cent. of lard oil greatly enhances the lubricative value of a straight mineral or blended oil, and this is present in many oils of this category.

Functions of Cutting Oils.

The functions of a cutting oil are well-known, but the relationship of these functions to basic operational data is worth mention. It is found that a shallow cut at low speed requires less cooling, and consequently less lubrication. Heavy cuts, also taken at low speed, need generous lubrication. With shallow cut, high-speed machining, marked cooling properties are called for, and on heavy cuts at speed the cutting oil must provide first-class cooling and lubrication. Thus soluble oils are the logical choice where the cooling factor predominates, although it is also true that their mineral and fatty-oil content now enables them to give a marked lubricating effect. Conversely, neat or straight-cutting oils should be used where lubrication is the primary requirement. Segregating the classes a little further, straight mineral oils are not usually satisfactory when machining metals of high tensile strength. The greater oiliness of the fatty oils makes them more suited for work of this nature. This characteristic explains the continued popularity of pure lard oil and blends of lard and mineral oils.

Requirements of Cutting Oils.

The desirable characteristics in either neat or soluble cutting oil are rather exceptional. I do not mean that they are merely extensive numerically, but that they are most exacting. With soluble oil, for instance, mention can be made of the following points which the manufacturer must carefully watch.

Soluble oil must emulsify quickly and permanently in all proportions from, say, 1 in 5 for turning high-tensile steels or such operations as tapping and broaching, right down to the extreme dilution of 1 in 100 as used for surface grinding. It should be capable of admixture to water drawn from vastly different geological strata which implies varying degrees of temporary and permanent hardness. Then it must store without loss of potency or emulsifying properties in humid England equally with the dry heat of the Transvaal or the extreme cold of Norway and Canada—this in itself is no mean requirement. In actual use, it is expected not to cause gumming of moving parts of the machine tool, nor to interfere with the bearings, nor to cause rust or stain on any of the multifarious metals with which it comes in contact. And here must be included, besides the 1001 different metals and complex alloys which can be machined with soluble oil, the ten or fifteen metals used in the construction of the machine tool which are located within the tooling area, and which normally are in constant touch with the main stream of coolant or are intermittently splashed with it. Then the water emulsion must possess real wetting properties, so that it is not flung off fast-revolving parts, but remains fully adherent, so that the process of refrigeration and lubrication is uninterrupted.

Whatever feed is provided, the emulsion must not froth, yet it is very difficult to avoid this when high-pressure delivery is given from narrow section pipes. Generous feed at low pressure is essential to secure the maximum service from any cutting oil, whether straight or water-soluble. With economy an essential part of production routine, large users wish to centrifuge the oil from metal turnings and swarf, and still expect the extracted coolant to be a serviceable product for re-circulation. The density of the emulsion must be such that even finely divided particles of metal, abrasive and grease—as produced in centreless grinding, for example—are capable of gravity settling-out, although in many coolant systems removal is effected by filtration or progressive sieving.

Then the welfare officer looks to the manufacturer to furnish a product which is quite innocuous to male and female operatives in varying degrees of health, and so dispel from his works the shadow of oil-cancer and dermatitis. It can be stated here that these pernicious diseases are more linked up with the operative than the oil, and that personal hygiene and good living are telling factors, with the cutting oil often the innocent carrier of germ infection introduced subsequent to manufacture. It is nevertheless true that these industrial diseases greatly concern the reputable manufacturer, so that he will deliberately select the constituent oils from those which are shown by recent research to have the least carcinogenic tendencies. Workers to-day are more particular about the smell of a product they are using, and with more factories being equipped with air-conditioning, this is natural. A soluble oil, when emulsified, must therefore not give off any objectionable odour or fumes in use.

Offset against the best endeavours of the soluble-oil manufacturer is the serious drawback that his product is never used as dispatched from the factory. A very simple mixing operation has to be performed by the user, and the service efficiency of the emulsified product is largely dependent on the manner in which this is carried out.

Tooling Requirements.

The cutting-oil manufacturer is continually receiving production reports which provide an interesting cross-section of tooling. In particular, it reveals the danger of generalization. Thus in machine-shop A 5 per cent. nickel chrome steel is being turned-on a given machine tool under soluble oil at 1 in 30 dilution, and excellent finish and tool life are obtained. The same operation is performed at identical feeds and speeds in machine-shop B, which finds straight sulphurized oil is the only medium that will give the finish desired, soluble oil at all dilutions proving unsatisfactory. This example typifies a position with which most production engineers are familiar. A great deal of uncertainty exists as to the behaviour of cutting oil, what happens when the tool is embedded in the workpiece and why one medium is better than another. The factors involved are so inter-related that at this stage it is difficult to assign a performance tag to individual cutting oils.

Phenomena arise in tooling which beg for explanation. Within certain limitations, lard oil is better than mineral oil for metal cutting, but why should this be so? If on account of its superior lubricating value, why should a journal bearing run hot when lard oil is substituted for mineral oil? In threading annealed copper pipe, ordinary sweet milk is sometimes used in preference to the whole range of manufactured cutting media. When machining aluminium, proportions of paraffin and water are being used in some quarters, Obviously, these neither mix nor emulsify, yet they service the operation satisfactorily. The function of sulphur in straight mineral or compounded oils is also difficult to explain. That its presence is beneficial is a proven fact, but whether sulphur additions tend directly to increase the cooling capacity of cutting fluids is a moot point. It is more probable that decreased heat generation is the relevant factor here owing to the reduction of friction made possible by the extra lubricative value of the treated oil. Sulphur does, however, increase the bite of cutting tools, and also improves the adherence of oils with which it is incorporated.

From the points mentioned, it will be apparent that the responsibilities of the cutting-oil manufacturer are many and onerous. They are consequently discharged with commensurate care. Although the industry has not yet succeeded in producing the universal cutting oil, manufacturers are sufficiently alive to tooling requirements to enable the known benefits of a coolant to be applied to almost every metal-cutting operation, thanks to the range of cutting media now offered.

CUTTING FLUIDS AND THE MACHINE TOOL.*

By A. H. Lloyd,† B.Sc., M.I.Mech.E., and H. H. Beeny,† M.Met.

The machine-tool manufacturer often has to guarantee the production of his machines, and the use of the correct cutting fluid may be an important contribution to his success. The chosen coolant will probably affect the rate of metal removal, the quality of the machined product in regard to finish and size, and the life of the tool.

Soluble oil emulsions possess great cooling power, so that the heat generated in cutting is rapidly eliminated, and metal can be removed more quickly than is possible with straight oils. The swifter cutting action is, however, associated with considerable wear of the cutting edge, so that these conditions are suitable only for simple types of tool which can be readily reground or replaced. The unique position of the hard carbide cutting alloys is dealt with later.

Experiments with emulsions on automatic and semi-automatic lathes using lower cutting speeds have failed, due to the rapid wear of form-cutters and multi-tool set-ups. It was found that screwing dies gave only approximately one-third of the life between grinds that was obtainable with a straight cutting oil of moderate quality; in addition, there is the danger of corrosion and the sticking of moving parts such as turrets and slides. It is now the definite policy of Messrs. Alfred Herbert, Ltd., to recommend a neat cutting oil for all automatic and semi-automatic machines. For similar reasons it is common practice to use a "straight" oil on machines performing hobbing, gear-cutting or other types of forming operation. In these cases the tools are costly, and any slight wear will affect the dimensions and finish of the machined product. The more expensive and intricate the machine and the tools, the greater is the argument in favour of the neat oil.

The high tensile steels much used nowadays in the aircraft industry, where great accuracy and smooth finish are demanded, impose severe conditions upon the cutting tool, and for threading it has been found really essential to use a super-fatted sulphurized straight oil as the cutting lubricant.

Apart from low cost, soluble oil emulsions have an appeal, owing to the absence of objectionable fumes and owing to the slight danger of the workers becoming affected by oil-acne or dermatitis. The surface finish given by such emulsions is frequently better than that obtained with the cheaper straight-cutting oils. Straight oils tend to fume, producing a close, oily atmosphere in the shop, and, in addition, there is the risk of dermatitis due to the oily liquid coming constantly into touch with the hands and arms of the workers. This danger can be largely countered by provision

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† Messrs. Alfred Herbert, Ltd., Coventry.

of an efficient oil-cleaning and sterilizing plant, and by providing a preparation which may be spread over the skin before commencing work. At Messrs. Alfred Herbert, Ltd., the oil itself is treated with a disinfectant to free it from harmful bacteria, and so prevent the conveyance of septic infection from one worker to another. It must be remembered, however, that oil dermatitis is frequently of a mechanical origin, the oil and dirt clogging the pores of the skin and preventing their effective action. Cleanliness on the part of the worker is undoubtedly one of the main requirements in keeping free from skin troubles of this nature.

A modern lathe is 50–75 per cent. heavier and 200–300 per cent. more powerful than its counterpart of five to ten years ago. This revolution in design was made necessary by the advent of the sintered hard carbide cutting alloys, but has proved to be of advantage with all types of cutting tool. These new hard carbide alloys, which will cut cast iron at 500 ft. per minute and many non-ferrous metals at 2000 ft. or more, naturally demand very high spindle speeds. The greater speeds tend to induce vibration, which is detrimental, as it breaks down the edge of the tool, causing chipping, whilst the hammer effect work-hardens the metal being cut and increases machining difficulties. A high degree of static and dynamic balance is required in the rapidly moving parts, whilst bearings need to be snug, with freedom from lift or end movement. The conditions for a lathe spindle are satisfied by the use of ball and roller bearings, which heat only slightly and resist wear, so that a close fit of bearings is maintained at all speeds for a long period of time. The Herbert machines use precision type of ball and roller bearings which have actually no running clearance, so that the spindle is rigidly held.

Automatic lubrication is now generally provided for the various units of the machines, and with increased pitch line velocities, hardened and ground nickel-chrome steel gears are necessary to withstand wear. Such gears are of high tensile steel, so that the face widths can be reduced and the supporting shafts shortened with improved resistance to deflection and vibration under load. Castings were re-designed to give greater rigidity in construction, and inverted "Vee"-shaped bed slides introduced to prevent any twisting tendency of chasing saddles or turret-slides under the pressure of the cut. Tool holders were made to support the tool firmly with a minimum of overhang. The shanks of the tools themselves are of robust section.

Greatly increased power is required to maintain the high spindle speeds with a steady feed, any tendency to stall under cut being usually fatal to carbide tools. A modern combination turret lathe is obviously more costly than its simple counterpart of years ago, and moreover, is constructed with greater accuracy. By reason of the points of design already enumerated, it is capable of cutting metals at a greater rate than a machine of less rigid and powerful construction, even with the same tools and cutting fluids, so that in considering the subject of cutting oils, one has to take into account the potentialities and special necessities of the machine upon which the work is to be done. These machines are expected to maintain their delicate alignments and good working condition for a long time, but are susceptible to serious damage by an unsuitable cutting fluid. The machine-tool manufacturer is in-

terested, therefore, in the choice of coolants made by the users of his products. Wear and corrosion are closely associated, and it is by no means always easy to convince a customer that loss of alignment is due to the action of the cutting fluid on the metal, and not to any shortcomings in the machine tool itself. Neat cutting oils preserve the machine from rust, and the moving parts exposed to the fluid are well lubricated; also if there is any leakage into headstocks or gear-boxes containing lubricating oil, the contamination is unlikely to do any harm, so that serious complaint of damage is very rare when a straight-cutting oil is used. The case is very different with soluble oil emulsions, as even those which gave reasonable service with earlier and simpler types of machine tool may now prove unsuitable.

With all aqueous cutting emulsions there is an inherent danger of corrosion, as the liquid consists largely of water, with a small quantity of oil held in suspension in the form of minute droplets. Soluble oil emulsions may, in fact, be divided into the many which cause corrosion on cast iron or steel parts either at once or after a period of use, and the very few which are satisfactory and cause rusting only under exceptional conditions.

Fig. 1 illustrates a syphon drip-test which has been developed in the Herbert Laboratory to determine the corrosive quality of cutting emulsions. Samples of the emulsions are placed in the conical beakers and are allowed to drip very slowly (about one drop per minute) on to the cast-iron block below, which is milled out into recesses. The block is made from metal similar to that used for lathe beds, and in each recess are placed small piles of brass and steel chips, so that workshop conditions are simulated, it being found that corrosion occurs most vigorously on a lathe where the chips collect as they fall from the cutting tool. The test is usually run for three or four days. Fig. 2 shows a typical result. The two left-handed surfaces are free from corrosion after being subjected to the action of fresh and used samples of a non-corrosive, soluble oil emulsion. The remaining recesses are rusted and tarnished by less suitable aqueous coolants. Our work in this field has made us realize that great care should be exercised in the choice of a soluble oil emulsion for general use in an engineering works, as some of the products offered on the market rust the machines at an alarming rate. Fig. 3 shows gears which have had the teeth practically eaten away by corrosion from a soluble oil emulsion.

About four years ago this problem of corrosion was thoroughly investigated. It was found that the addition of nickel, chromium and copper, either separately or together in proportions which could be employed commercially in heavy lathe bed castings, did not afford protection. A well-known oil company was approached, and ultimately a cutting fluid was produced which gave a slightly *alkaline* liquid when mixed with water. In this emulsion the oil is suspended in a condition corresponding more closely to true solution, and the liquid is clear or opalescent when first put into use, instead of being milky in appearance. After over two years of practical experience with this newer type of cutting fluid, the position is very satisfactory, as rusting has been obviated on the machines and the soluble-oil bill has been actually reduced in relation to the output. This achievement is partly due to the great stability of the emulsion, as if water is set free, rusting follows inevitably. The stability of the emulsion

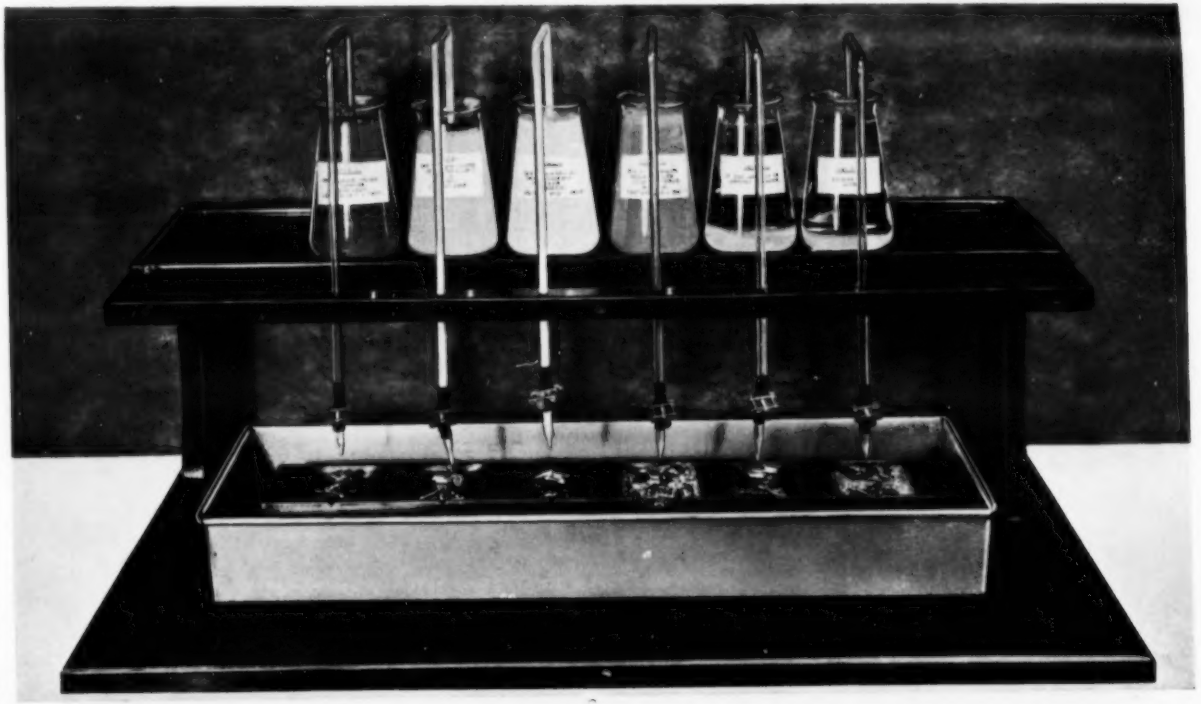

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FIG. 1.

SYPHON DRIP-TEST TO COMPARE THE CORROSIVE ACTION OF VARIOUS GRADES OF AQUEOUS CUTTING FLUID ON CAST-IRON LATHE BED METAL.

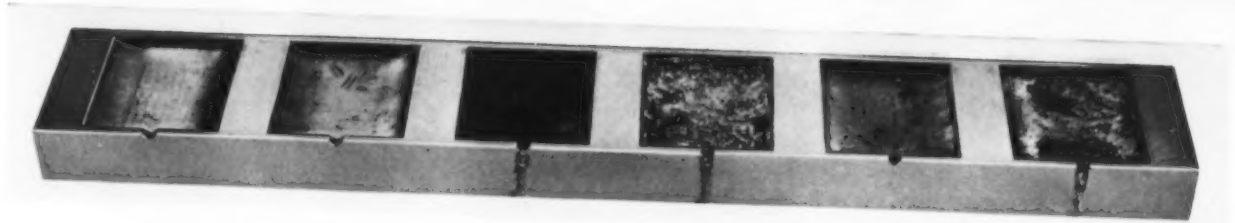


FIG. 2.

CAST-IRON BLOCK MADE FROM BED METAL, SHOWING EFFECTS PRODUCED BY COMPARATIVE CORROSION TESTS.

FIG. 3.

STEEL GEARS AND SHAFTS SEVERELY DAMAGED BY CORROSION DUE TO A SOLUBLE OIL EMULSION.

also enables high dilutions to be used, and it is now recommended to mix 1 part of oil with 40 parts of water; even so, tests up to a period of six months show that the strength of the mixture continually increases, so that after a month or so the mixture may contain only 15 parts of water to 1 part of oil. This strengthening takes place notwithstanding the addition of stock fluid at the original strength to compensate for loss of volume due to evaporation and splashing. The neat oil mixes readily with either hard or soft water to form a non-corrosive fluid, but as an additional precaution it is beneficial to dissolve 0·5 per cent. of common soda in a hard water, such as that found in the Coventry district, before adding the oil. This addition precipitates calcium and magnesium salts, which would otherwise combine with some of the emulsifying soap in the oil and form compounds which rise to the surface as a scum. Made up in this way, the cutting fluid will remain stable through many months of use, whereas with the milky emulsions previously employed, breakdown into water plus oil would frequently occur after only two or three weeks' service.

A number of clear types of soluble oil are now marketed, but a careful selection should be made, as some of these are prone to cause corrosion. The test illustrated by Fig. 1 is very valuable for trying out various products, and when one has been selected, the method can be used to ensure that the quality is maintained in every delivery. Due to the complex nature of soluble oil emulsions and to the fact that the characteristics can change during use, the laboratory tests on fresh grades of oil should always be supplemented by thorough trials in the machine shop.

It should be pointed out that there is one form of rusting caused by evaporation and condensation which cannot at present be avoided with any water-bearing cutting fluid. Soluble-oil emulsion has been known to leak into a housing containing gears or other steel mechanism and produce rusting, even though the parts affected were well above the level of the liquid. A curious example of this action is seen when a lengthy steel part, such as a spindle, becomes rusty at the end farthest from the chuck while machining is in progress, due to the steam or vapour generated by the heat of cutting condensing on the colder metal.

Cutting tools have to resist abrasion, heat and stress, both static and dynamic, in proportions varying according to the cutting conditions and the type of metal being machined. It is the important function of cutting fluids to absorb the heat and provide a lubricant to neutralize as far as possible the abrasive effect. High-carbon tool steels resist abrasion and stress well, and are still used occasionally when it is necessary to hold a very keen edge. Such tools soften very easily under cutting heat, so that they greatly depend on the cooling property of the cutting medium; soluble oil emulsions are therefore used in preference to oils, but, even so, only low cutting speeds are attainable.

High-speed steels have great resistance to shock and stress, so that they are robust and are able to take heavy cuts on materials such as tough steels, nickel and Monel metal, which form continuous ribbon-like chips of great strength, and which consequently set up heavy pressures on the face of the tool. Much frictional heat is also developed, and although a high-speed steel tool will cut for a short time at a dull red heat, coolant fluids are essential to efficient and speedy production.

Fig. 3. STEEL GEARS AND SHAFTS SEVERELY DAMAGED BY CORROSION DUE TO A SOLUBLE OIL EMULSION.

In requiring a cutting fluid, high-speed steels differ from the sintered hard carbide tool materials, which appear to cut as well dry as in the presence of a fluid. These tools have, of course, a phenomenal resistance to abrasion, combined with a hot-hardness exceeding that of high-speed steels; they lack only toughness, but this weakness can be countered, as already explained, by mounting and using the tools so as to protect them from excessive shocks or vibration. Emulsions are frequently used on turret lathes with these tools, but are provided for the benefit of the high-speed steel drills or other tools included in the equipment. If used alone on a modern lathe, either on steels or non-ferrous metals, dry cutting is the general practice, as the tools cut perfectly well under such conditions, and again, as spindle speeds are very high a cutting fluid tends to be scattered violently by the centrifugal action of the chuck and the work.

Grey cast iron is turned at lower speeds ranging between 180 and 500 ft. per minute, so that an emulsion might be employed to cool the work and wash away chips, but unfortunately in this case a fine black dust is produced which rapidly fouls the liquid and forms hard masses wherever settlement occurs about the machine.

As more powerful and rigid machine tools find their way into engineering shops, there will be more and more scope for the hard carbide alloys, themselves improved and elaborated, and consequently less need for cutting fluids. Does it not seem that there will come a day when cutting fluids will almost be banished from the machine shop, and will no longer splash over machines and men?

THE SELECTION OF CUTTING FLUIDS.*

By H. J. Mason.†

The problem of the correct selection of cutting fluids for use in modern engineering shops is one which should be called upon to be solved by the works laboratory. With keen competition among the oil suppliers and the general desire of all executives to increase production with lower processing costs, it is essential that processing materials should be scrutinized in order that their true " value for money " may be assessed.

The writer believes that in the past many a good contract has been won or lost by someone's " personal opinion," without any basic facts or figures to substantiate that opinion, and it is thought that few products have been more influenced by that personal opinion than cutting fluids.

In this paper, therefore, the writer attempts to outline some practical tests which have been carried out over the past three or four years, and by which the efficiency of cutting fluids has been determined. The results, since obtained on large-scale production of accurately machined parts, have amply proved the accuracy of those tests.

Types and Uses of Cutting Fluids.

Cutting fluids, generally, fall into two classes :—

(*a*) Water-emulsion and water-miscible oils.
(*b*) Straight-cutting oils.

Under the latter heading can be included the many varieties of sulphurized oils, fatty compounded oils, straight mineral cutting oils and the more modern chlorinated oils.

With regard to the specific uses of any particular type of cutting oil, and always bearing in mind the " value-for-money " aspect on which the selection of cutting fluids must be based, it is as well to explore the complete possibilities of the use of the water-emulsion or water-miscible oils before the more costly straight cutting oils are used. It must be acknowledged straight away that there is no hard-and-fast rule as to when either type should be used, but generally speaking it is preferable to use a water-emulsion or water-soluble oil, in view of their comparative cheapness and cleanliness. To the writer's knowledge this type of cutting fluid has been successful on almost all types of machining operations, like drilling, turning, hobbing or broaching.

Some actual machine features dictate that a straight cutting oil be used, as, for instance, in the case of machine construction being such that a cutting fluid leakage drips on to an electric motor. In this case, of course, a water-soluble fluid would cause an electric short circuit. Again, machine construction may be such that the cutting fluid will penetrate

* Paper presented for discussion at the One Hundred and Eighty-third General Meeting of the Institute of Petroleum held on 11th October, 1938.
† Messrs. Vauxhall Motors, Ltd.

into the functional parts of the machine itself, with the result that were a water-soluble fluid used, bearing seizure might occur; but these instances are the exception rather than the rule. They are quoted here to show that individual machine features must also be considered in the selection of a cutting fluid, as well as the actual machine operations.

One particular machine operation has, however, been found to require special consideration, and that is in connection with the manufacture of helical gears and the operation of tooth-shaving of these gears to make the correct tooth form.

The operation of tooth-shaving is performed essentially on a serrated rack tool, which meshes with the gear to be shaved in such a manner that the axes of the gear and the rack make an angle of about 30°. When the rack is moved along its axis, it drives the gear, and the action is therefore partly shaving and partly burnishing, and the contact between the tool and the tooth is a straight line.

Under these conditions—and this seems to apply to any machining operation in which some burnishing action can be traced—the best results are obtained by using a 100 per cent. fatty oil. Indeed, the function of a cutting fluid in this particular operation is one which seemed to demonstrate the peculiar difference between "oiliness" of a fatty oil and high film rupture strength of a sulphurized or chlorinated oil, in that the latter two types of oil produced a very badly torn tooth form, as compared with a smooth finish obtained with a fatty oil, when tried out on this shaving operation.

In the description of the tests which follows, the same procedure, from a practical point of view, can be followed for water-emulsion or straight cutting oils, and some special tests applicable to one or the other types are also given.

Test Procedure and Results Obtained.

To the production engineer one of the obstacles which impedes the flow of finished parts from any machine is tool deterioration, and when this reaches the point beyond which components are not being correctly made, it is necessary to break down the machine and either re-grind the tool or replace the worn tool by a new one.

On many modern machines this "setting-up" with a new tool is a relatively lengthy procedure, hence the fewer the stoppages for this purpose, the more efficient is the output. On these practical trials, therefore, it was decided that, since the major function of a cutting fluid is to prevent tool wear and the subsequent re-grinding and re-setting, and if other variables could be reasonably controlled, the recording of *the number of parts machined per "set-up"* should give an accurate evaluation of the efficiency of the cutting fluid.

These variables to be controlled were each a responsibility of a separate department in the organization, and were controlled as follows :—

1. Tooling	Tool Inspection Dept.
2. Machining feeds and speeds . .	Production Planning Dept.
3. Material composition and physical characteristics of parts to be machined .	Metallurgical Dept.
4. Accuracy of finished jobs . . .	Inspection Dept.

The record of number of pieces per tool-change was logged by the Group Inspector in the normal course of his duties.

Some serious consideration was given to the machining operation on which the tests were to be performed, and it was decided to base results on Hobbing operation of gears and gear-box mainshafts, for the following reasons :—

(*a*) The finish required on gears is the highest which is expected from a pure cutting method.

(*b*) Machining operations had been previously well established and considerable experience obtained with cutting fluids on that job.

(*c*) The machines used in the test were single-purpose type and a steady supply of uniform forgings was assured.

(*d*) The breakdown point of the tool could be fairly accurately established, for, owing to the fact that certain limitations are imposed on the design of hobs, and the clearance angles are small, hence any rubbing, as distinct from cutting on the sides of the gear teeth, could be easily observed both by visual inspection and by measurement.

A series of tests on straight cutting oils was carried out and the following constants were maintained :—

Operation.

Finish hobbing mainshafts.

Machining Feeds and Speeds.

Speed	84 r.p.m.
Cut	0·050 in. feed per rev. of work.

Material.

Nickel molybdenum steel.

Composition :

Carbon	0·38–0·43%
Nickel	1·80–2·10%
Molybdenum	0·25–0·30%
Manganese	0·60–0·80%
Sulphur	0·05% max.
Phosphorus	0·04% max.
Silicon	0·15–0·30%

Physical condition :

Annealed pearlitic structure.

Hardness :

Brinell numbers	241–207
Diameter of impression	3·9–4·2 mm.
Approximate tensile	45–50 tons per sq. in.

Grain size :

McQuaid-Ehn	5–8

Summary of Results.

Data taken on approximately four weeks' run on each oil and average of data on three machines on each oil :—

Oil No.	No. of Set-ups.	Components per Tool-Change.		Average.
		Max. Recorded.	Min. Recorded.	
1	12	400	144	191
2	14	393	165	259
3	27	399	105	168
4	40	275	98	126
5	40	340	240	280

Further data were then considered necessary on oils 2 and 5 in order to ascertain if any real difference could be found.

A second series of tests was then conducted on the same nickel molybdenum steel, and these revealed a consistent average of 35–40 cuts per position of hob.

On gear finishing, however, a difference in the finish machined surface was noticed in the shape of tears along the pitch line of the tooth-face. It is to be noticed that this occurred on a softer type of material and details are as under :—

Operation.

Single-cut hobbing on a rigid hobber.

Machining Feeds and Speeds.

Speed . . . . . 150 r.p.m.
Cut . . . . . 0·040 in. per rev. of work.
giving a cutting speed of 139 ft. per min.

Material.

Composition :

Carbon	0·10–0·14%
Nickel	4·50–5·20%
Chromium	0·10% max.
Manganese	0·30–0·40%
Sulphur	0·04% max.
Phosphorus	0·04% max.
Silicon	0·30% max.

Physical condition :

Pearlitic.

Hardness :

Brinell numbers . . .	207–163
Diameter of impression . . .	4·2–4·7 mm.
Approximate tensile . . .	38–44 tons per sq. in.

Grain size :

McQuaid-Ehn 5–8

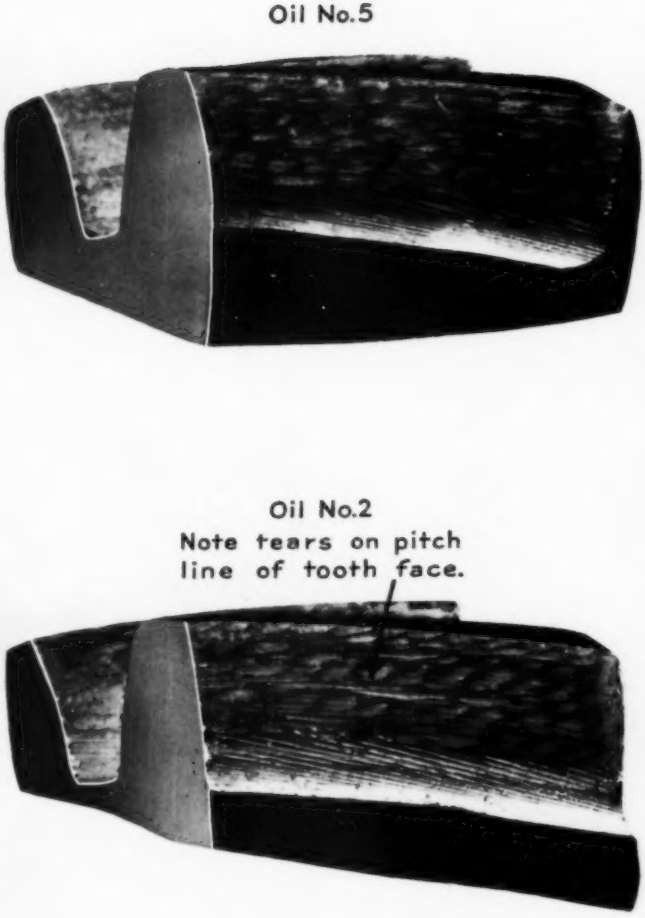


FIG. 1.

[*To face p.* 658.

FIG. 2.

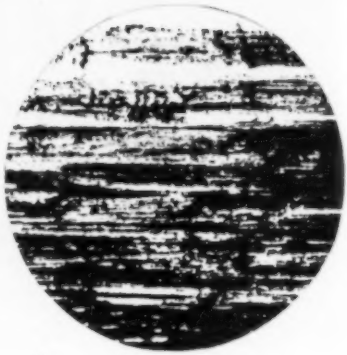


FIG. 3.

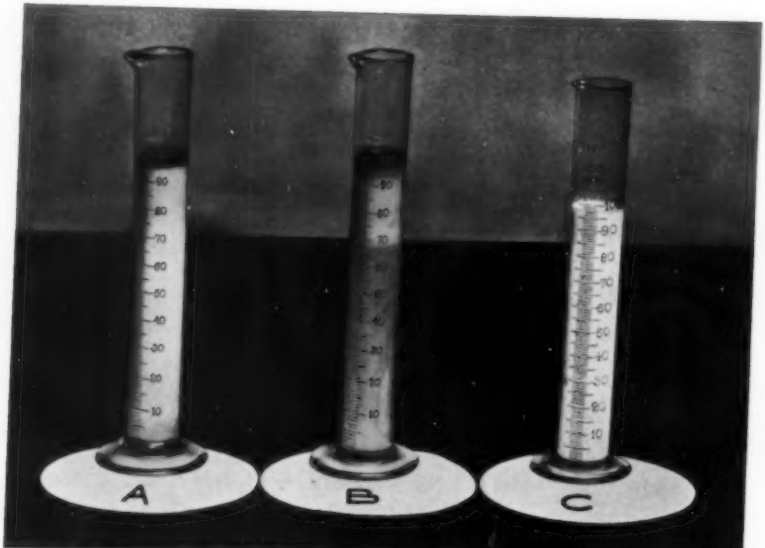


FIG. 4.

Results obtained as recorded by photographs are shown in Figs. 1, 2 and 3.

Fig. 1 shows examples of helical gear teeth. The tear marks on the machined face as produced with Oil No. 2 are quite distinct when compared with the clean-cut surface which was obtained with Oil No. 5.

Figs. 2 and 3 are reflected light photomicrographs of teeth from the same cutting tests; the tear marks are more easily distinguished.

Characteristics of Oil No. 5, giving the best results, are as follows :—

Composition : A mineral oil compounded with a sulphurized fatty oil.

Saponifiable oil	20%
Total sulphur	1·80%
Mineral oil	remainder

Physical characteristics.

Sp. gr. at 60° F.	0·902
Viscosity :	
70° F.	435 R. secs.
140° F.	76 R. secs.
Flash point :	
Closed	350° F.
Open	365° F.
Acid value	4·5 mg. KOH per gm.
Film strength :	
Almen value	5000 lb. per sq. in.
Almen value (after heat test)	7000 lb. per sq. in.

The heat test referred to was introduced in order to determine the deterioration—if any—of the oil when subjected to higher temperatures, and is performed by heating 200 gms. of oil in a 400-c.c. beaker in an oven at 200° F. for 48 hrs. In the beaker 1 gm. of finely powdered iron is placed to accelerate any sludging tendency.

The 7000 lb. per sq. in. Almen value was obtained after that test, and the cause for the rise in that value is not explained. It is sufficient evidence, however, to indicate that the high film strength is not destroyed under conditions of heat such as are likely to be developed under cutting conditions.

Laboratory Tests.

It is submitted that the practical tests performed gave the answer to the group of major functions of cutting fluids—viz., to cool the work and prevent excessive tool wear, to ensure a good finish of accurate dimensions, but the less obvious functions need some laboratory check.

These functions and their tests are detailed below :—

(*a*) Freedom from tendency to form rust on machine or components.

(*b*) Stability under working conditions. This chiefly applies to emulsion type cutting oils.

(*c*) Non-injurious to operators.

Determination of Rusting Tendency of Cutting Fluids.

(*a*) *Visual Test.*

Approximately 3 gms. of freshly dry-machined cast-iron chippings are cleaned and dried in alcohol–ether mixture and then transferred to a shallow watch-glass. They are then covered with a sample of the emulsion or oil to be tested and after a minute or so excess of the sample is drained off. The wetted chippings are then exposed to normal room atmosphere for 24 hrs., when any rust which has developed on the chippings can be seen.

(*b*) *Quantitative Rust Test.*

This tendency to rust can be reduced to actual figures by the determination of the $Fe : Fe_2O_3$ ratio in the treated chippings, a successful method of which is as follows :—

A weighed amount of the "rusted" iron chippings are washed in alcohol–ether mixture and transferred to a beaker and digested for 15–30 mins. with copper sulphate solution and one or two c.c. of $N/1$-sulphuric acid. The metallic iron in the chippings thus passes into solution. The whole is then filtered and the iron is estimated in the filtrate by precipitation with NH_4OH in the usual way, care being taken to eliminate any excess copper by H_2S.

The metallic-iron content in the rusted chippings can be calculated and the iron oxide estimated by difference.

Determination of Emulsion Stability.

The breakdown of soluble-oil emulsions is largely due to the hardness of the water used as a diluent and the agitation caused by pumping and splashing during the actual machining operations.

Since soluble calcium salts are those most widely occurring in hard water, a laboratory method for the determination of emulsion breakdown is as follows :—

Make an emulsion with the oil under test and of suitable dilution as is used on machines—usually 20 : 1, in water containing 0·1 per cent. solution of lime water. Shake the whole vigorously for 10–15 mins., and allow to stand for several days. Separation of the emulsion can be seen, and is depicted under the above condition of test in oils *A* and *B* in Fig. 4.

It is interesting to note that oil *A* on this Fig. gave a complete separation during the practical tests on a machine after three weeks' use.

Health Hazard to Operators in Contact with Cutting Fluids.

This characteristic is one which must not be overlooked, nevertheless it is one which the writer considers is often unnecessarily connected with cutting fluids, and he refers to skin dermatitis or oil rash. It is obviously beyond the scope of this paper to offer any medical advice in this direction, but it is well known that dermatitis is a disease which seems to attack certain individuals more than others, and is largely due to the

de-fatting of the skin by oil acting as a solvent or by the irritation of the skin by fine metallic particles suspended in the cutting fluid.

To test a cutting fluid in this connection is impossible, but referring to water-soluble cutting oils, they should be free from excess alkali or irritating disinfectants and for straight cutting oils excess of free fatty acid should be avoided.

Finally, the writer would like to make it clear that the observations and data given in this paper were arrived at during the normal course of events in an engineering works laboratory for the sole purpose of selecting suitable cutting fluids for use, and the data concerning the many types of oils which have been tested over the last three to four years are not available, because, having due regard to price and performance, they were not considered value for money.

He would also like to tender his best thanks to the Directors of Messrs. Vauxhall Motors, Ltd., for permission to publish results and photographs appearing in the paper.

THE FUNCTIONS OF CUTTING FLUIDS.

By Prof. H. W. Swift,* M.A., D.Sc., M.I.Mech.E.

Having regard to the fact that swarf is one of the chief products of the engineering industry, it is surprising that we know so little of the mechanism of its production. The incompleteness of our understanding of the action of cutting tools generally and the lack of agreement between experts on many of the problems of cutting-tool practice are due mainly to the large number of variable conditions which are imposed by industrial needs and mask the basic principles of cutting action. Of these conditions the use of cutting fluids is but one, and the engineer may perhaps be forgiven if he has neglected to study it fully, in his preoccupation with such matters as tool material and form, speeds and feeds, economics of cost and quality, and in his attempt to keep pace with the new working materials and tool metals which are continually becoming available. Whatever the reason, the mechanism of cutting-fluid action has lacked systematic study in this country, and for what information we have we are largely dependent on the work of Boston and his associates in America.

Any understanding of the functions of cutting fluids must be based on an appreciation of the mechanism of cutting itself, and to this problem workers in this country have in the past made notable contributions. In the light of this work it is possible at least to form some picture of the cutting processes on which the action of cutting fluids will need to be superposed. In a short paper it is clearly impossible to analyse each cutting process in its relationship to cutting fluids. It is proposed, therefore, to consider only basic principles, to present some account of the mechanism of cutting, to inquire how a cutting fluid might facilitate this mechanism and to what extent these facilities are provided by the cutting fluids at present available.

Action of a Cutting Tool.

With the possible exception of grinding wheels, all metal cutting tools are fundamentally related to a basic form, and for simplicity the planer tool may be regarded as their prototype. The essential geometrical features of this tool in its relation to the work are the cutting edge (C), the cutting angle (α) and the clearance angle (β) (Fig. 1). In order to obtain a picture of the cutting action, we shall assume, for reasons which will be clear later, that a chip has just broken away from the work, leaving an oblique plane of fracture CD. As the tool moves forward relative to the work, the material just in front of the point C is penetrated and crushed by the point of the tool, and at the same time is sheared along the plane CZ.

* Sheffield University.

(*a*) If the crushed material is brittle, it disintegrates and is expelled, leaving the tool in the position shown in Fig. 2*a*. At the same time the resisting force on the tool has increased, and with it the stress in the uncut strip C_1D, which is under compression from the tool, and consequently in shear on oblique planes. As the crushing process continues,

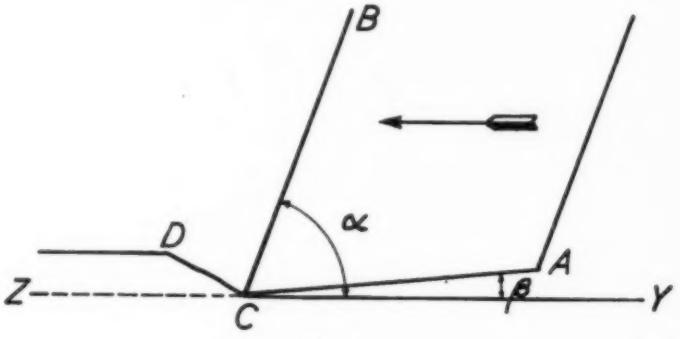


FIG. 1.

the shear stress increases with the tool force, until a point is reached where the material fails across a plane C_1D_1 of maximum shear and the chip C_1D_1D is ejected. The cycle of operations then repeats itself with C_1D_1 as the new surface for attack.

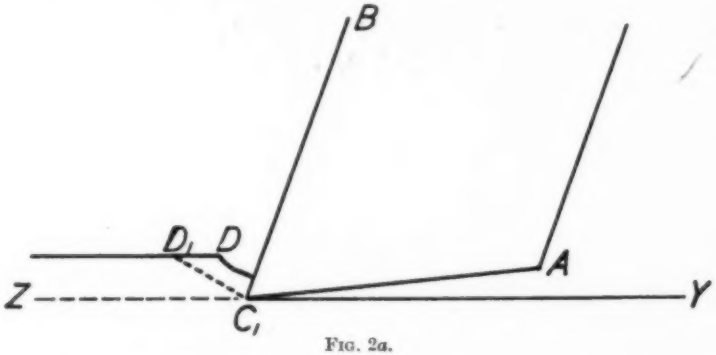


FIG. 2*a*.

In this case the face CB of the tool is under pressure near the edge C, but relatively little sliding movement occurs on this surface. The point C also presses into the work normal to its surface YZ in so far as is necessary to clean or burnish any asperities left by the shearing action. A certain frictional loss is therefore involved by the burnishing action, as well as by the expulsion of swarf. The main absorption of energy, however, is in disintegrating the material of the work.

(*b*) If the material is not brittle it does not disintegrate at the commencement of the cycle, but forms a badly distorted pad, and shears away from the body of the work at C_2, as indicated in Fig. 2*b*.

As this pad develops, the resultant thrust from the tool increases in value as before, and its line of action moves away from the line YZ as indicated. This produces a condition of combined tension and shear at

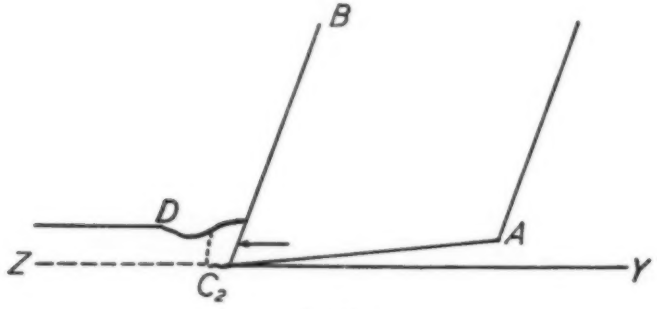


FIG. 2*b*.

the end of the incipient crack at C_2, which therefore tends to extend as indicated at C_3 in Fig. 2*c*, and a system of compression with its induced shear on oblique planes in the uncut strip C_3D_3.

As this action proceeds, if the material is ductile the pressure of the tool face will bend the heel E of the incipient chip (Fig. 2*d*) away from the body of the work, opening and further extending the crack C_4 as the tool

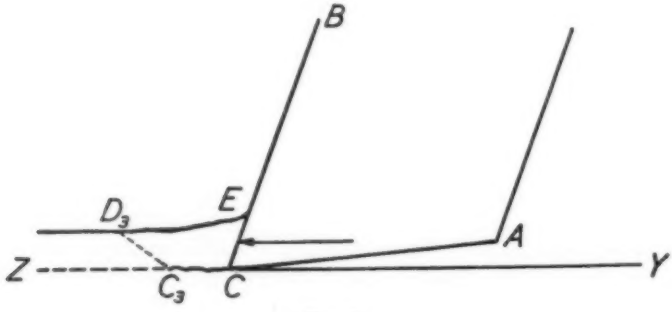


FIG. 2*c*.

advances. In this way a shaving begins to form and to curl away from the face of the tool. The crack C_4 may not extend regularly, however. After an initial extension the bending action occurs under a reduced tool pressure, which may be insufficient to continue the crack. As the tool then moves forward, it first bends the chip (Fig. 2*e*), but as it approaches the end of the crack the bending action gives place to shearing, with its

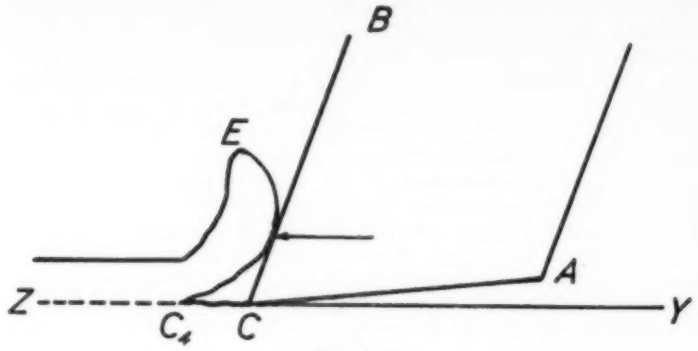


FIG. 2*d*.

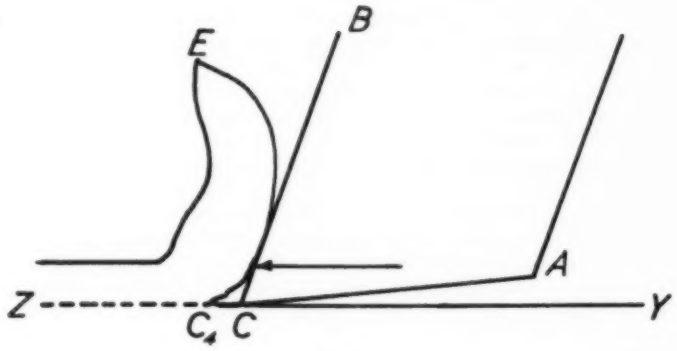


FIG. 2*e*.

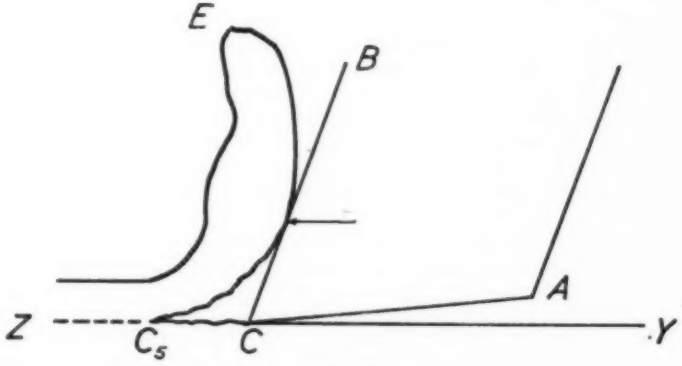


FIG. 2*f*.

increased resistance, slipping occurs along some plane through C_4 and the crack extends from C_4. This relieves the pressure by allowing bending to recommence (Fig. 2*f*), and the cycle continues, producing a shaving which is more or less severely sheared and corrugated near its outer surface, but smooth on its inner surface, owing to the burnishing pressure of the tool face as it is rubbed along it. Although the face of the chip is also burnished, however, the surface YZ may be left with more or less regular "chatter" marks, corresponding to the cycle of fluctuating action, and therefore bearing some relation to the depth of the cut. The length to which the shavings develop depends on the residual strength of the sheared sections; in most cases they will break at some point remote from the seat of operations, probably where they press on the work after curling back.

In some cases, particularly with deep cuts in a not very ductile material and with large cutting angles, the crack extension at C_3 (Fig. 2*c*) may be delayed, with the result that the chip is sheared off along a plane such as C_3D_3 before the bending process has fully developed, and short, partly curled chips are the result. In other cases, with very ductile material, smaller cutting angles and higher cutting speeds, the cutting process is more nearly continuous, long, strong shavings are formed and a regular surface is left on the work. As with brittle metals, the work surface of the crack C_3 is cleaned and to some extent burnished by the edge C of the tool as it follows up, and a normal force necessary to carry out this function exists between the tool edge and the surface YZ.

In this cutting process friction occurs with great pressure and considerable sliding on the face of the tool, burnishing friction occurs at the tip of the tool, and a great deal of work of deformation is converted into heat as the chip is sheared, torn and bent. The smaller the cutting angle the less will be the bending strain, the more efficient the splitting action on the crack, the less intermittent the shearing and thickening of the chip and the smaller the cutting force required.

Lubrication and Cooling.

Let us now consider in what ways a suitable fluid may assist in the mechanism of cutting as sketched above. In the first place, there is clearly an opportunity for considerable saving by lubrication if a suitable lubricant can be found. The work of actual deformation of the chips is largely an intrinsic property of the metal itself, and cannot therefore be substantially affected by lubrication. In a general way it is to be expected that those metals which have high strength and ductility and which are greatly distorted in the process of cutting will absorb more energy of deformation than others, although this is not as yet fully substantiated by test.

Frictional action of more ordinary type occurs between the face of the tool and the chip or shaving, and between the tip of the tool and the surface which it burnishes. The forces which give rise to these two components of friction are difficult to determine separately, but tests [1] indicate that with the cutting angles normally employed the two forces are of the same order for ferrous metals, whilst for brass and copper the burnishing force is considerably less.

From figures obtained by Stanton under certain experimental conditions for nickel steel and cast-iron at appropriate cutting angles we find, if we adopt his suggested value of 0·35 for the coefficient of friction, that the total resistances to the tool under comparable conditions were 250 and 212 lb. respectively, whilst the effective frictional resistances were 128 and 85 lb., leaving "deformation resistances" of 122 and 127 lb. respectively. It is interesting to note, in passing, the rather remarkable fact that the actual work of deformation was practically the same in the two metals, although their mechanical properties are markedly different. Other resistance figures from the same paper suggest that the total work of cutting would be sufficient, if no heat went elsewhere, to raise the general temperature of the steel chips about 1000° F., and of the cast-iron and brass turnings rather less. The actual work of deformation would account for a temperature rise of the order of 500° F., and friction for the remainder. Of the work of deformation a certain proportion passes to the stock, whilst the frictional work is divided between the chip, the stock and the tool, the last receiving a double share. Owing to the high local frictional temperature at the points of contact of the tool with chip and stock, it is unlikely that any appreciable fraction of the heat of deformation passes to the tool. So far as the tool is concerned, therefore, the heating is largely due to friction, and this also applies in the main to the stock. On the other hand, the heat carried by the chips is mainly due to deformation, and only in a lesser degree to friction.

From the standpoint of efficient cutting the condition of the chips is secondary to that of the tool, and also less important than that of the stock. It must also be remembered that heating tends to be cumulative in the tool, whilst the chips and to some extent the stock are continually carrying their heat away. The primary function of a cutting fluid is therefore to limit the temperature of the tool. This can be effected either by prevention or cure; the frictional heat passing to the tool can be reduced by lubrication, or the temperature rise due to the heat generated can be reduced by the cooling action of a circulating fluid. In principle, prevention is better than cure, and effective lubrication would not only reduce the temperature of the tool and the stock (minimizing distortion), but would also reduce the power required for cutting and promote continuity of chip formation and so improve the work. On the other hand, under the drastic conditions imposed by cutting, efficient lubrication is much more difficult to achieve than efficient cooling, and except with light duties and low speeds (where the failure of lubrication would have no serious consequences) there is greater safety in a coolant than in a lubricant. There is, of course, greater virtue still when the two functions can be combined in a single fluid. A fluid which provides efficient lubrication and cooling will not only perform the essential functions of increasing tool life and performance; it will also reduce power consumption, prevent distortion of the work, improve accuracy and finish, and will also help to remove chips where necessary.

The perfect cutting fluid has (*pace* sundry manufacturers) not yet appeared. Its essential properties are a high specific heat, fluidity and good lubricating properties. Its subsidiary requirements are mainly negative; it must be non-corrosive, non-injurious, non-inflammable and stable.

The cutting fluids in common use fall into four groups; aqueous solutions, aqueous emulsions of soluble oils, straight oils (mineral, fatty or compounded) and "doped" oils (containing sulphur, graphite or other addition). Of these the solutions and weaker emulsions have specific heats about twice those of the oils and about ten times those of the ordinary metals. Good fluidity also assists heat disposal by convection, and here again the aqueous groups are superior, water being a hundred times more fluid than an ordinary machine oil at ordinary workshop temperature. On the other hand, surface tension, which adversely affects the wetting and penetrating power of a liquid, is three times greater for water (and still more for aqueous solutions) than for ordinary oils.

The lubricating property of a liquid under the drastic pressure and surface conditions prevalent in metal cutting cannot be assessed by ordinary bearing standards. Viscosity, for instance, is no index of this property. It is essentially a surface as distinct from a mass property, and for that reason the "active principle" need not be in concentrated form. The efficacy of sulphur and graphite, for example, which has been demonstrated in a number of cases, is not materially improved by additions beyond a certain small proportion. Up to the present time no correlation has been established between the efficacy of a cutting lubricant and any other physical or chemical properties, and the only satisfactory method of assessment is by direct test with a cutting tool.

Cutting Fluid Tests.

Two kinds of test have been applied in connection with cutting properties; in one the endurance or performance of the tool is determined, and in the other the cutting force or power. The former test takes account of cooling as well as lubricating conditions, whilst the latter is essentially concerned with the effects of lubrication. Systematic investigations of cutting forces with various fluids have been carried out by Boston [2] in drilling, planing and turning operations and he has also made performance tests in sawing and turning.

He found that drill torque was reduced by suitable cutting fluids in all cases except free-cutting brass. The maximum reductions were from 7 per cent. with free-cutting steel to over 30 per cent. with carbon steels and aluminium. The most effective fluids were sulphurized oils. Water and emulsions were useful with nickel-chrome and high-carbon steels, but otherwise straight oils were better. Planing tool tests on the nickel-chrome steel gave a similar order of merit to the drill tests on this material, although the greatest saving in power was 15 per cent. instead of 22 per cent. In lathe tests on a low-carbon steel the sulphurized oils again behaved well, as did also those oils containing lard-oil. The maximum diminution in cutting force was 15 per cent. Lathe tests on the nickel-chrome steel also showed the advantage of sulphurized oils, but water and emulsions were found ineffective.

In considering these figures it will be appreciated that since the work of deformation is largely unaffected by improved lubrication, the diminution in friction is much greater than the percentages shown.

Performance tests on a machine saw with various metals showed a time

saving in cutting under fixed conditions up to 45 per cent. with a sulphurized oil, and this oil also did well in a dulling test. Other fluids varied somewhat in their behaviour with different metals, a light mineral oil being on the whole the least satisfactory. Endurance tests on a lathe turning nickel steel showed that for a tool life of 20 minutes aqueous solution and emulsions allowed an increase in cutting speed of about 25 per cent. and mineral oils about 15 per cent. In similar tests on a nickel-chrome steel cutting speed increases were about 15 per cent. with soda-water or sulphurized oil, 10 per cent. with emulsions and rather less with mineral oil. Colloidal graphite in water showed little advantage, but colloidal graphite in oil emulsified with water or diluted in plain mineral oil gave results superior to any of the other fluids. The most effective cutting fluid was found to depend on the prescribed tool life, and for lives shorter than 13 minutes the greatest cutting speeds were permitted by aqueous solutions.

In order that a cutting fluid shall be effective it must be applied in the proper quantity and in the right way. Generally it is considered that an ample flow at a moderate velocity provides the most efficient cooling action, although Burley [3] found that variations of stream velocity for a given flow had little effect, and in some cases where the fluid is relied on to remove swarf (as in deep drilling) a high velocity is advantageous.

There are also certain cases where the volume of coolant may properly be restricted. Apart from certain metals and operations for which the use of a cutting fluid is unnecessary, there are certain conditions under which efficient cooling may prove a disadvantage. Dempster Smith [4] found that a cutting emulsion reduced the life of a tool when taking *fine* cuts on carbon steel, owing to its quenching action on the heated surface pearlite, and it has been suggested that too efficient cooling may restrain the flow of surface molecules necessary to produce a high finish. It has also been found that the life of a tool increases as its temperature is raised up to a certain point. Hence a coolant is inadvisable under conditions which do not heat the tool above its optimum temperature.

The cutting fluid should, of course, be applied as close as possible to the point where the cooling action is required, and it has long been the general practice with lathes to apply the fluid to the chip at the point of its removal from the stock. If, however, as argued above, the primary object is to cool the tool, it would appear that either a lateral stream on to the tool, or one in the direction *B* in Fig. 3, should better achieve this object. There is direct experimental evidence in favour of the direction *B*, for Burley [5] found that while a given flow from *A* improved the tool performance by 34 per cent., the same quantity from *B* improved it by 70 per cent. He also found that up to a certain point the improvements due to two streams *A* and *B* were cumulative when they operated together.

The lathe tool presents the most difficult problem, because its action is continuous, its cutting speed often high and its duty onerous. In a planer the action is intermittent and the speed generally lower. In the case of a milling cutter the action of any one tooth is intermittent, there is ample room to apply fluid and each tooth can carry its own supply of lubricant to the work. In cases where finish is important the amount of heating is generally small, and the cooling problem is quite secondary to

lubrication; fortunately so, for efficient cooling would be difficult to arrange in such processes as screwing, tapping and broaching. In this respect grinding is an exceptional case; here cooling is the only function of the fluid—lubrication would merely destroy the bite of the wheel—and since the dimensions of the finished work are important, it is the work quite as much as the wheel to which the coolant should be applied.

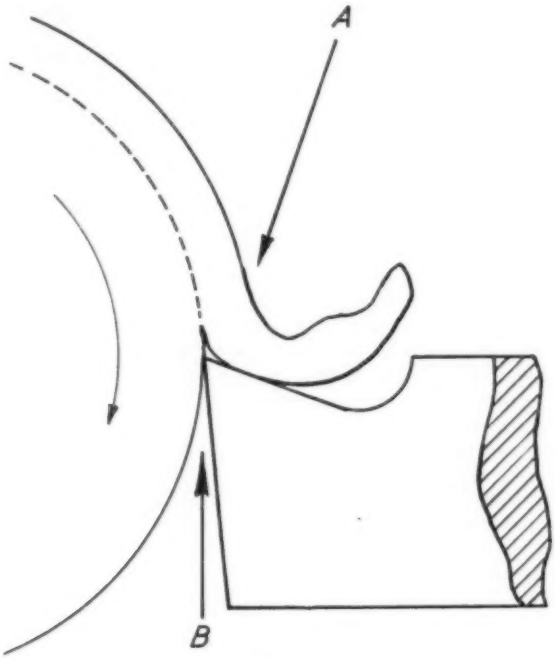


FIG. 3.

CONCLUSIONS.

1. The limited data available appear to show that the heat of chip deformation and the frictional heat are of the same order, but the heating of the tool itself is due mainly to friction.

2. There is experimental evidence that a slightly sulphurized oil has better anti-frictional properties than other fluids for which data are available.

3. For purposes of heat dissipation, aqueous solutions and emulsions are superior to oils.

4. Conditions in practice vary so widely that no single fluid is likely to fulfil all cutting requirements. An emulsion with sulphonated oil base, provided it were stable and non-tarnishing, would appear to have prima facie claims to consideration for most purposes.

5. There is need for a systematic study of the mechanism of action and the overall performance of cutting fluids under controlled conditions representative of practice.

References.

[1] Stanton and Hyde, *Proc. Instn Mech. Engrs*, 1925, pp. 182, *et seq.*
[2] Boston, *Trans. Amer. Soc. Mech. Engng*, 1932, M.S.P. 54—2; 1933, R.P. 55—1; 1934, R.P. 56—5; 1936, R.P. 58—11.
Boston, *Trans. Amer. Soc. Steel Testing*, 1933, p. 623.
[3] Burley, *Proc. Instn Mech. Engrs*, 1919, p. 814.
[4] Dempster Smith, *ibid.*, 1925, p. 392.
[5] *Loc. cit.*

DISCUSSION ON CUTTING OILS AND MACHINERY.

THE One Hundred and Eighty-third General Meeting of the Institute of Petroleum was held at the House of the Royal Society of Arts, John Street, Adelphi, W.C.2, on Tuesday, October 11th, 1938, at 5.30 p.m. COLONEL S. J. M. AULD, O.B.E., M.C., D.Sc., President of the Institute, was in the Chair.

THE CHAIRMAN said that he welcomed the gathering that evening as evidence of the great interest taken in the important subject of cutting oils. The Institute was to be congratulated on having such a range of papers on cutting fluids presented before it. This series appeared to him to be complete. It covered manufacture, use—from the point of view of production and the machine-tool maker—and a discussion of the theory of the function of the fluid.

THE CHAIRMAN said that the meeting was intended by the Institute of Petroleum to mark the inauguration of the Lubrication Group. The choice of papers for such an occasion was worthy of its importance, and reflected credit on its organizers.

He then asked Mr. Elliott A. Evans to make a short statement regarding the Lubrication Group.

MR. E. A. EVANS said: Exactly a year ago over 600 people expressed their interest in lubrication, through the medium of the General Discussion on Lubrication and Lubricants, which was organized by the Institution of Mechanical Engineers with the co-operation of thirty-one British and twenty-two Dominion and Foreign scientific societies. The sales of the *Proceedings* of that international meeting have made it perfectly clear that lubrication is a very popular subject. This may be attributed to the many fields of science which compose the estate. The danger, however, of working on such an estate is that of becoming parochial. Workers must have an imperial spirit, aided by some uniting machinery through which information can be passed.

The Council of the Institute of Petroleum has taken the initiative in forming a Lubrication Group, and I have the honour of being its first Chairman. The function of the Group is to advance our knowledge of lubrication and lubricants. It is important, therefore, that any one, whether he be chemist, physicist or engineer, who is interested in any phase of this subject, shall enrol as a member of the Lubrication Group.

The following papers were then presented:

"The Manufacture of Cutting Oils," by John F. Miller (*see* p. 645).

"Cutting Fluids and the Machine Tool," by A. H. Lloyd, B.Sc., M.I.Mech.E., and H. H. Beeny, M.Met. (*see* p. 650).

"The Selection of Cutting Fluids," by H. J. Mason (*see* p. 655).
"The Functions of Cutting Fluids," by Prof. H. W. Swift, M.A., D.Sc., M.I.Mech.E. (*see* p. 662).

DISCUSSION.

THE CHAIRMAN said it had been their intention that the discussion should have been opened by Dr. Merritt, Director of Design at the Royal Arsenal. Unfortunately Dr. Merritt could not be present, and he (the Chairman) thought that all present would appreciate his suggestion that the discussion be opened first by the Chairman of the Lubrication Group, Mr. E. A. Evans.

MR. E. A. EVANS said: The work which was done at the National Physical Laboratory some years ago, at the instigation of the Institution of Mechanical Engineers, interested me so much that I was terribly disappointed when it was discontinued. The beautiful illustrations which appear in the paper by Stanton and Hyde are brought back to memory by Professor Swift. These illustrations prove at a glance that machining of metal is not a simple operation. By a special steel block the surface of the metal is pushed off. The tool merely splits the metal by brute force, pushes the torn piece away, and then slides over the rough torn surface with sufficient force to smooth out the irregularities. This operation is so commonplace that we may be inclined to accept it without further question.

We are now stimulated to inquire further, What relationship has the geometry of the tool to the direction of the crack and the burnishing of the roughened surface? What is the relationship between metallic structure and machinability? Do all metals behave alike? If we can answer all these questions, and others besides, is the engineer any better off financially?

The petroleum industry is not primarily interested in engineering practice, but the two are so intimately related that they must keep in step. The problem under review embraces the resources of many branches of science. Dr. Bowden has studied friction. Professor Finch has revealed hitherto unknown facts about polishing. Professor Adam's work on the spread of fluids on surfaces is allied to cutting operations. Medical science has, alas! been called in to deal with occupational diseases of the skin.

The importance of this subject is emphasized by the fact that the Institution of Mechanical Engineers recently invited Professor Schlesinger to present a paper on Machine Tool Tests, and in March 1939 that Institution will be giving still further consideration to this absorbing topic. [*Applause.*]

PROFESSOR FINCH (Imperial College) directed attention to the fundamental aspects of lubrication, and pointed out how the effectiveness of a lubricant was a function of the ease with which the long-chain oil molecules could yield to a shearing stress by leaning over in the appropriate direction. He also spoke of the important rôle played by the hard and amorphous oxide film formed on the bearing-metal surface in the presence of an E.P. lubricant.

MR. M. COOPER (The Hoffmann Manufacturing Co.) said he felt they had received such a fund of useful information during the short space of time they had been at the Meeting, that there must certainly be ample

choice of subject on which to offer comment. It seemed, from the excellent description of the manufacture of soluble oils given in the paper by Mr. Miller, that the requirements of cutting compounds were well understood, particularly with regard to their lubricating, cooling and rust-proofing qualities; and also the avoidance of any harmful effect to the operator or the machine. Personally, he thought that in dealing with practically any cutting operation of metals, one had to arrive at the most suitable compromise. There were many variables which were liable to effect the results in conflicting ways, and it was only by carrying out a lengthy series of tests, as described by Mr. Mason, that one could select the best oil or emulsion for the particular operation, due regard being paid to the economic aspect.

He could sympathize, too, with the machine-tool maker who was keenly interested in maintaining a high standard of performance of his products, which could be seriously affected by the use of unsuitable compounds, largely on account of the close association of wear and corrosion.

The risk of injury to health of the operator also required consideration, care being taken to avoid any affection of the skin, such as by irritation or extraction of the natural fat, and the presence of harmful bacteria. Any disinfectant used must be selected with care, and the removal of finely divided swarf and other foreign matter in circulation became necessary. Stability of the emulsion was essential, and freedom from objectionable odour after a period of service was also an item of some importance.

If all these features were obtained, there still remained one most important factor in maintaining a clean bill of health—namely, personal cleanliness of the operator. Perhaps this side of the subject was reminiscent of the horse in the proverb of old which could be easily led to the water, but could not be persuaded to drink.

Mr. A. E. Lawson (Vacuum Oil Co., Ltd.) said: Starting with the paper by Mason, we find an accurate record of two similar operations, which were hobbing using straight sulphured and compounded oils. The author states that the observations were taken over ordinary working conditions, and doubtless form a valuable guide to the performance of the various straight oils tested. Before reaching the tabulated results, we are informed that there is no hard-and-fast rule as to when a soluble or straight oil should be used, and success has been obtained on soluble oil on the same type of operation—that is, hobbing—and as a considerable amount of hobbing is done on soluble oil at Mr. Mason's organization, it would be of interest to hear his remarks on the comparative results obtained on the two types of cutting media. There cannot be a great difference in the materials for automobile gear and shaft construction, and the circumstances surrounding a possible change within the 3–4 years' period would be of value. As the hob is an expensive tool, generally operated on a straight oil, unanimously agreed by the other authors as being the type needing protection, the life or output between grinds on soluble is a matter of great concern. The finish of the work, as there is invariably a grinding, shaving, or similar operation to follow hobbing, is important only as far as surface inequalities are not greater than the amount of metal left for the final operation to remove.

A single-operation machine of the type required would also appear to come within the ban on solubles suggested by the machine-tool makers, Lloyd and Beeny.

In connection with laboratory testing by these gentlemen for the anti-corrosive value of emulsions, my experience has been that results on the laboratory and on the machine are not always parallel, and I suggest that corrosion, particularly of the work, is more liable to occur under heavy cutting conditions when the operation is such as to restrict the flow to the tool-point. Local heating tends to a steam formation and a splitting of the emulsion. A reduction in the chip-loading usually cures the trouble, or an increase in emulsion strength, both awkward suggestions to make to a machinist attempting to get high output or soluble-oil economy.

Miller mentions the wide divergence of straight and soluble cutting-media found necessary on supposedly similar operations and materials. My belief is that the conditions are never actually the same. It is seldom that machinists disclose all information, such as tool material, top and side rake, whether the steel has been correctly—or if at all—normalized, if soluble was at correct emulsion strengths or, with straight oils, whether proper filtration to remove fine metallic suspensions had been carried out.

Swift's illustrations of the tool in cut are conventional and, as we are aware, diagrammatic. I would point out that even the single tool like the planer or turning tool cuts not only at the face, but also at the side. It is here that the greatest compressive stress is experienced, and I consider it an illusion to imagine any considerable fissure preceding the arrival of the tool. In heavily loaded tools the pitting is witness of the load near the side cutting-edge. In heavy cuts there will be a certain opening and, as cutting speed is low, time is given for the cutting media to flow.

In conclusion 2, "There is experimental evidence that a slightly sulphurized oil has better anti-frictional properties than other fluids for which data are available," I disagree with this. The research of my organization is in agreement with the various authors that the fatty content of a straight-cutting oil assists the reduction of friction between the chip and the tool. This tends to impart an even rupture from the main stock instead of alternations of loading, and so promotes fine surface finish. Varying proportions of sulphur increase the load-carrying capacity or extreme-pressure value, and prevent actual fusion or welding of fine particles of metal to the tool face, which destroy the surface over which the chip has to pass. It is significant that the free-cutting or high-speed machining steels are invariably of high sulphur content.

Particularly in connection with steels, I feel that insufficient consideration is given to the gap between ultimate strength and yield point. A high ultimate strength of brittle type of metal imposes little frictional load on the tool, thereby inducing little heat, but the same ultimate strength in a ductile steel imposes a heavy load and continuous rubbing, with considerable thickening of the chip, indicating a high degree of plastic flow. This type will require the more highly fatted and sulphurized oil.

To revert to the term used by Miller of "wetting the surface," I am in some doubt as to whether this is intended to mean a mechanical or chemical attachment.

I disagree with many of the tests which have been carried out on drills and saws, which were probably for convenience or economy, as such—and perhaps on the fringe may be hobbing—do not give a good datum line on which to base an estimate of other cutting-operation requirements. The only good standard is plain turning, which will be found satisfactory on aero-engine cylinders at certain proportions of fat and sulphur in mineral oil. For finning, on the same component, speeds are reduced to about 35 per cent. and fat and sulphur content increased, with viscosity lowered to ensure penetration in deep grooves. Fat to ensure no tearing of thin ribs of metal and extra sulphur to prevent welding. Broaching, if long compared with diameter, requires much sulphur; grooving, low viscosity; tapping, high viscosity and much compound; gear shaping, low viscosity to permit oil "dwell" on short surfaces, and so on; but with sufficient investigation parallel with practical experience, for specific operations, at least, we should be able to chart our cutting oils as we do lubricants for other services, making an omnibus recommendation for multi-operation machines on similar metals, and specific recommendation as expedient for single operations if expense of special tools, requirements of finish, etc., demand it.

A final word about grinding, which Swift indicates has only a cooling requirement. The latest grinding practice on thread grinding can be speeded to 60 per cent. increase by the use of a low-viscosity compounded mineral oil. This does not grease the wheel, and permits crush-forming the wheel profile instead of single-point trimming, so effecting further considerable time-saving. This is an additional indication of the necessity for continuous and correlated investigation of cutting problems as affected by oils and coolants, and of the need for blending old principles with new methods.

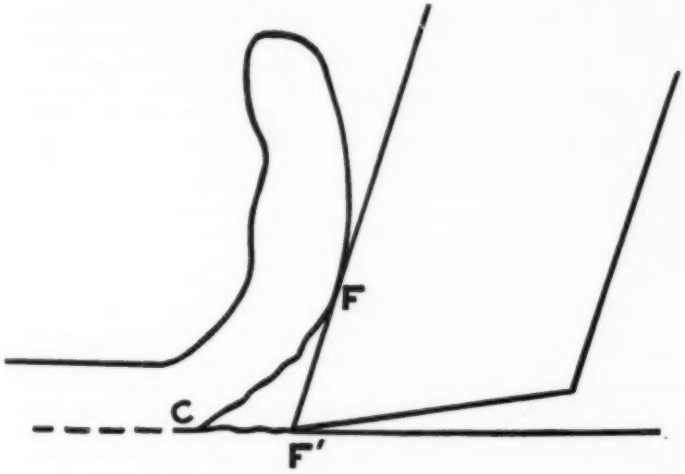
Dr. J. C. Bridge (Home Office) said he knew little about cutting fluids, and although he had pleasure in saying a few words, he would not detain the meeting for more than the three minutes allowed by the Chairman.

Many speakers had referred to dermatitis, a subject nearly as complicated as cutting fluids, and about which it was difficult to say much in a short time. There was this, however, he would like to say. One of the speakers had referred to cancer of the skin, and he thought the occurrence of this disease from cutting fluids was negligible.

With regard to dermatitis itself, he had always maintained, and still felt it true to say, that there were a certain number of individuals who, no matter what they came into contact with, would contract dermatitis. Of the others, cleanliness of the skin was of primary importance in the prevention of this condition. This necessarily implied adequate facilities for keeping the skin clean. He thought the first object to be aimed at in the prevention of dermatitis was the proper use of soap and water.

Dr. P. Bowden (University Chemical Laboratory, Cambridge) said he felt very diffident at speaking because, prior to this meeting, he knew so little about the theory and practice of cutting. He had, however, been so interested in, and had learnt so much from, the papers just presented, that he felt bold enough to take part in the discussion.

He was particularly grateful for the very clear analysis of the mechanism of the process which had been given by Professor Swift. As the meeting will remember the work of cutting was divided into two main parts. The first part which occurred in the region C was the work necessary to tear away and crush the metal. The second part was the frictional work required to slide the tool over the metal, at the rubbing areas of contact



FF'. Professor Swift has pointed out that the work of cutting might be about equally divided between these two processes. It is the frictional work at *FF'* which is mainly responsible for heating the tool. It is in connection with this second part of the process—the frictional part—that he would like to mention three points.

The first point was connected with some experiments which Mr. Leben had carried out recently at Cambridge.* These experiments showed that the frictional force between moving metals is not constant, as is usually supposed, but is fluctuating very violently. The metal surfaces do not slide continuously: they stick together for some time, and then a sudden very rapid slip occurs. *They move along by this process of "stick and slip," and an intermittent clutching and breaking away of the metals is occurring all the time.* It was well known, of course, that the cutting metals became hot, and some years ago Mr. Herbert † had shown that the temperature of the cutting tool was high. In Cambridge we had been interested in the temperature of sliding surfaces, and here experiment had shown ‡ that the surface temperature of the sliding metals might be very high indeed. The local temperatures at the points of contact exceed 1000° C., although the mass of the metal appeared to be cool. A more detailed analysis of the surface temperature showed that this, too, was fluctuating in a similar

* Bowden and Leben, *Nature*, 1938, **141**, 691; *Proc. Roy Soc.* (unpublished).
† Herbert, *Proc. Inst. Mech. Eng.*, 1926, **1**, 289.
‡ Bowden and Ridler, *Proc. Roy. Soc.*, A., 1936, **154**, 640.

manner to the friction. *The instant that "slip" occurred there was a sudden very rapid rise and fall in the surface temperature.* The whole temperature flash might be over in less than a thousandth of a second.

The fact that the motion proceeds in jerks is important because it meant that the momentary stresses (and temperatures) were correspondingly greater and the surfaces are torn and damaged when slip occurred. Now, Mr. Leben has found that the magnitude of the "stick slip" is greatly influenced by the relative physical properties of the moving metals, particularly by their relative melting points. For steel (m. pt. *ca* 1300° C.) sliding on steel, for example, the slips were relatively large, but with molybdenum (m. pt. 2470° C.) on steel the stick slips were very much smaller, and the motion was smoother. It is possible that this effect may play a large part in the cutting process. The experiments suggest that a large difference in melting point is an advantage, and that the metal of the cutting tool should be carefully chosen so that, in combination with the other metal, *it shows small stick slips in its frictional behaviour.* Such a combination might give smoother and easier cutting.

The second point is concerned with the magnitude of the friction between the rubbing metals. The value for the coefficient of friction used in the calculations quoted in Professor Swift's paper is 0·35. This is not very different from the values usually found for the friction of unlubricated metals. No matter how carefully metals are cleaned in the air, there will always be present on their surface an adsorbed film of oxide, water vapour and other contaminants. It is very difficult to remove this film, and most friction measurements on so-called "clean metals" were really made with metal surfaces covered with this layer. Recently Mr. Hughes * in Cambridge has succeeded in getting clean surfaces by prolonged heating of the metal in a very high vacuum and has measured the friction of naked metals. When the last film was driven off, the friction was enormously increased, and the *coefficient of friction between really clean metals may be some twenty or thirty times as great as that between metals "cleaned" in the ordinary way.* In the cutting process the metal is being continually torn away and a fresh surface exposed. At the moment of formation this surface may really be clean, and consequently its friction may be very high indeed. The bare surface will, of course, become contaminated by oxygen or by the cutting fluid, but if the rate of cutting is high, this may not occur quickly enough and the frictional losses and damage may be considerably greater than is usually supposed.

The third point referred, not to the metals, but to the cutting fluid. As the previous speakers had pointed out, this had many onerous duties to perform. One of its functions was to reduce the friction. The process of stick and slip previously described was very general, and occurred in the presence of mineral oils and many lubricants. Certain molecules were, however, able to prevent this stick slip and allow continuous sliding to occur. Such substances might be useful in cutting fluids. Some large molecules, such as the long-chain fatty acids, were quite good lubricants. These were usually arranged on the surface in a regular manner to form a film in the way that Professor Finch had described. It should be emphasized, however, that this arrangement took time and a big, long

* Unpublished.

molecule which lumbered up to the surface might need to turn round before it could attach itself. In cutting particularly, where a fresh surface was continually being exposed, *speed of formation of the film* was important. It might be useful to use smaller molecules which could nip in quickly and attach themselves firmly to the surface.

Mr. Romney (W. B. Dick & Co.) said he did not propose to go into the abstruse subject of the theory of cutting lubrication, but wanted to mention some of the minor points in the papers which, he felt, required amplification. First, he would like to ask Mr. Miller to give further details as to his differentiation between what he called finely dispersed emulsions and clear solutions. He had been under the impression that all the clear solutions, which were more or less opalescent, might be regarded as, roughly speaking, colloidal solutions. Mr. Miller obviously did not mean the milky type of emulsion when he referred to finely dispersed emulsions, so that his method of differentiation from clear solutions would be of interest.

He did not agree with Mr. Miller's contention that the clear solutions caused gumming on slides, and knew of solutions which did not have that effect, particularly if the dilution were kept fairly constant. That brought him to another point in connection with the clear soluble types, and it was a point to which Mr. Beeny had referred in his paper. The clear type of solution tended to strengthen in service, whereas emulsions weakened. This would appear to be due to the fact that in the case of emulsions the oil could be fairly readily adsorbed by swarf, whereas the chief loss with clear solutions, apart from splashing, was by evaporation of water.

The speaker congratulated Mr. Miller on his care in using for his products only non-carcinogenic mineral oils, but would like some enlightenment on Mr. Miller's method of selection. He knew, of course, of Dr. Twort's work at Manchester, and might explain to the meeting that Twort had developed a formula relating refractive index and specific gravity to carcinogenic properties, but he understood that at a later stage Twort had himself expressed doubt as to the validity of his formula. If Mr. Miller had any inside information on the latest position, would he be good enough to impart it to the meeting?

The speaker said Mr. Miller had made a rather dangerous suggestion in mentioning the importance of good living by the workers in the prevention of dermatitis. The term was a rather loose one, and if the Trade Unions noted the remark, they would probably see the opportunity for demanding increased wages for operatives.

There had been a reference to the effect of sulphur in cutting oils. This had been explained to some extent, but he hoped that discussion would bring out opinions on the value of film strength in cutting operations. Sulphur had been extensively used to increase film strength in extreme-pressure lubricants, but it was by no means the only material which had that effect, and if it were established that film strength were an important feature, there were quite a number of compounds, apart from the chlorinated ones which had been mentioned, which might give better results.

Mr. Mason had referred to laboratory tests, and the speaker was particularly interested in these. Mr. Mason had developed a quantitative rust

test, and the speaker thought this scarcely necessary or desirable. In the laboratory to which he was attached they carried out rust tests, and their basis of differentiation was whether an oil rusted at all, or not. They rejected oils which gave the slightest trace of rust. He rather doubted whether Mr. Mason was able by his test to differentiate between what he would call good oils and excellent oils, although he could probably cut out very inferior oils. He did not think the control in most rust tests sufficient. A considerable amount of work had been carried out in his laboratories on this subject, and in view of the variations in shop and laboratory atmospheric conditions from day to day, they had been carrying out rust tests under carefully controlled conditions. Solutions and emulsions of various concentrations were spotted onto plates of various metals, or piles of metallic turnings, and such factors as the temperature, humidity and purity of the air and rate of drying of the spots carefully controlled. It was also possible to watch the effect of contaminating the air with deleterious gases which might be found in some workshops.

Mr. Mason mentioned an oxidation test in which oil was oxidized in the presence of 1 gram of iron powder. It was desirable, in such a test, to standardize catalytic conditions by keeping the powder in suspension by some such means as controlled blowing, otherwise there were bound to be variations in surface, depending on the settlement of the iron powder. Mr. Mason mentioned an increase in film strength as the result of oxidation. This was feasible, since it was well known that some oxidation products increased lubricating power as measured by friction tests, and they might have a similar effect on the film strength.

Finally, the speaker wished to know whether Mr. Mason's laboratory tests had placed the five oils he had tested in exactly the same order as his four weeks' practical tests, which were the tests he really based his conclusions on. If not, did he use his four weeks' test to keep abreast with all modern developments in cutting oils? It was essential for them to get down to really sound laboratory tests, otherwise the job of buyers or the technical advisers to buyers of firms using cutting oils, in selection, must be more or less guesswork.

Mr. D. Clayton (National Physical Laboratory) said: Looking at this subject from the point of view of engineering research, it is apparent that the problem has been "roughed out" in the course of the practical use of cutting fluids, and in the experimental work that has so far been carried out. To make further progress to real efficiency, however, it is now necessary to face up to the much more laborious task of close examination of all the factors that enter into this complicated problem, and of detailed experimental work.

In efficiency is included the attainment of satisfactory finish and precision of dimensions in a minimum number of operations, as well as the more obvious long tool-life, low power-consumption, quick removal of material, etc. There is also the incorporation of the required qualities for the many materials and cutting conditions in as few fluids as possible.

As regards the physical properties, many points have been mentioned, but it may be remarked that viscosity should be low to promote local turbulence at the tool for better heat removal, and to allow easier flow

into narrow spaces as in tapping, for example. High latent heat of evaporation is not to be forgotten where the supply of liquid is limited.

Whilst tool cooling in a general way is obviously necessary, I wonder, from analogy with the fact that hard steel often wears better when not of maximum hardness, whether the tool should always be as cold as possible. As regards cooling the chip, it must be accepted from E. G. Herbert's work that there are optimum temperatures for efficient removal, so cooling must not be indiscriminate; the deformation characteristics (ductility, work-hardening qualities, and so on) in relation with temperature must be taken into account.

It has been recognized that not only is there friction between the chip and the tool, but the pressure may be sufficiently high to lead to " scuffing ": hence the extreme-pressure characteristics of many cutting oils. This is not only a question of tool life because of removal of material, but one of heat generation, because the tangential force will go up for a time to some five times its normal value when " scuffing " occurs. It follows that progress with cutting fluids is likely to be made hand in hand with advance in extreme-pressure lubricants. In connection with this extreme-pressure consideration, an interesting feature of some tests in the four-ball apparatus is that, with emulsion, mild wear will occur when with certain oils scuffing would take place; this might explain certain anomalies found in practice. Moreover, a suggestion in a German paper on the effect of cutting fluid on finish depends on this phenomenon. With an oil, the built-up edge forms on the tip of the tool and the direction of the fissure ahead of it is slightly inwards to the work; a rough finish on the work results. With an emulsion, wear rapidly takes place just behind the tool edge, the top rake of the tool becomes effectively increased locally, the direction of the fissure ahead of the tool becomes tangential to the work and a smooth finish results.

Increase of oiliness would be expected to improve the finish, for the reaction along the chip towards the work due to friction between the chip and the tool would be less, and the effect is equivalent to an increase of top rake angle.

Considering, finally, the investigation of cutting fluids and their action, the practical use in actual cutting tests is inevitable for immediate choice, but the variables are so numerous, and it is so difficult to make sensitive measurements, that this method cannot be recommended as adequate in a long-range investigation. The only hope seems to lie in an analytical approach: assessing the influence of the physical properties of the fluids, investigating friction, wear and scuffing, and then checking at significant points with practical tests. Any interdependence of the properties of the fluids and such factors as tool angles would, of course, require practical tests for their elucidation.

The fundamental phenomena of friction, wear and scuffing present the main difficulty, as in a number of other lubrication problems. Good progress is being made by a number of workers in experimental work on these phenomena, but it must be admitted that not very much in the nature of agreed results has yet been achieved. As regards friction, it is not enough to measure its static value at ordinary temperatures: the range of temperatures at the tool tip must be covered and under kinetic conditions.

These temperatures can be found from practical tests using the tool and work as the two elements of a thermocouple, the method employed by E. G. Herbert in this country, by Gottwein in Germany, and by Shore in U.S.A. It may be remarked incidentally that, in connection with scuffing, there is an opportunity here for those extreme-pressure testing machines which, because of their plain sliding motion instead of combined sliding and rolling, are subject to criticism as regards gear lubricant testing.

THE CHAIRMAN said: I think you will all agree that the papers to-night have been of a high standard, and have well fulfilled the purpose of stimulating useful discussion.

Time does not permit of any judicial summing up on my part, nor, for that matter, of any appreciable contribution to the discussion. That may well come later. It has been made quite clear, however, that this is a subject where the understanding of the underlying theories and the needs of the user are essential to the oil technologists and to manufacturers of cutting fluids. It emphasizes the need for meeting on common ground and discussing the problems from every aspect.

I have, therefore, very much pleasure in proposing a hearty vote of thanks to the authors of the four papers and to the Chairman of the Lubrication Group. [*Applause.*]

The Meeting was then closed.

MR. G. H. THORNLEY (C. C. Wakefield & Co. Ltd.) wrote: Mr. Miller seeks explanation of the function of sulphur in cutting fluids; its beneficial effect, either chemically combined or as a suspension of elemental sulphur in oil, is well established. It has been stated (in advertising matter) that sulphur is the ideal lubricant because instead of becoming more fluid with rise in temperature it actually increases in viscosity. This is quite true between 115° C. and 180° C., but above 180° C. the viscosity of molten sulphur decreases up to the boiling point at 444·5° C. Is it not more probable that sulphur acts as an anti-welding agent as the active sulphur is supposed to function in extreme-pressure lubricants? The position of chlorine is doubtless similar. The chlorinated solvents would make excellent cutting-fluid adjuncts for difficult machining operations were it not for the toxicity of their vapours and their decomposition with liberation of hydrogen chloride under the action of heat and light.

Mr. Mason reports, in connection with tooth shaving of helical gears, that when any burnishing action can be traced in a machining operation, then 100 per cent. fatty oil yields the best result, and sulphurized or chlori nated compounds give a badly torn tooth form. An explanation of this phenomenon would be very interesting. The exact meaning of the burnishing process is not quite clear; it apparently differs from cutting and from the extreme-pressure, high-speed rubbing action of hypoid gear, which demands active sulphur/chlorine combinations to avoid scuffing or tearing of the metal.

The difficulty of evaluating soluble-oil emulsions is well known, and Mr. Mason's remarks on the subject are welcomed, but one might suggest that a rusting test exposed to " normal room atmosphere " requires a little refinement. A laboratory atmosphere is subject to extraordinary changes

in concentration of acid and other corrosive fumes, so that in a test seeking to compare rusting tendencies of various emulsions at different times, some standardization of atmosphere is essential.

The views of users on the desirable viscosity of the basic oil in soluble oils would be useful. Most soluble oils are based on mineral spindle oil, with or without a proportion of fatty oil. The *apparent* viscosities of these can often be varied greatly by gel formation, dependent on the percentage of water incorporated in manufacture. Soluble oils of truly high viscosity can be prepared on a very viscous mineral-oil base, and it would seem that oils of this nature, in which extreme pressure-resisting properties can be incorporated, should hold certain advantages for difficult machining operations.

Mr. Harry Shaw (Consulting Research Engineer, Whitworth) wrote: In these papers dealing with the various aspects of cutting, frequent reference has been made to finish, but no definite data on finish have been presented. The finish judged correctly is a good indication of the nature of the cutting action, and approach to the breakdown of the tool edge is indicated by the change in the finish. Indeed, the finish can be used as an indication of the cutting conditions.

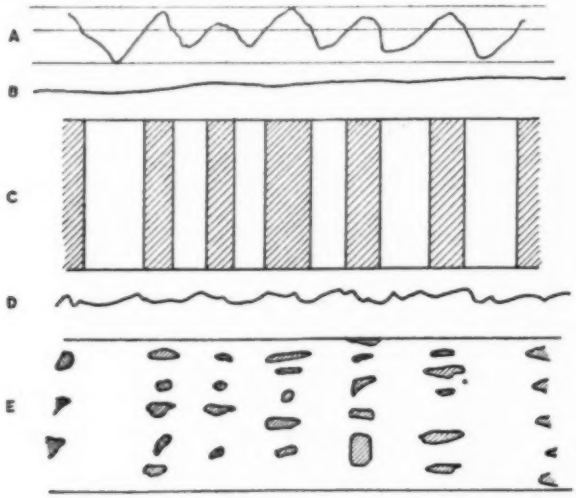


Fig. 1.

Judgment of the finish by eye is not sufficient, but an instrument such as the Shaw Contorograph * for actually recording the shape of the surface roughness is necessary.

Tests were carried † out on mild steel and Phœnix free-cutting steel using Wimet tools cutting dry, with soluble oil, mineral oil and colloidal graphited mineral oil. Most of the actual cutting tests were carried out

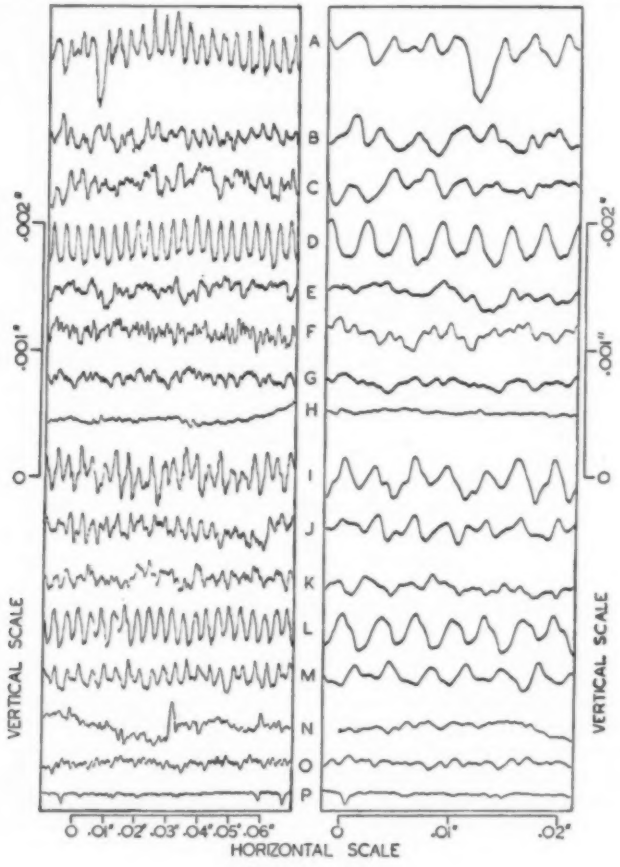
* Shaw, *J. Inst. Prod. Eng.*, **10**, No. 8.
† Ibid., *Mechanical World*, **104**, p. 389.

by Mr. Percy Holmes at the works of Steel, Peech & Tozer, Ltd., Sheffield, whilst the mineral and graphited mineral oils were supplied by E. G. Acheson, Ltd., London.

TABLE I.

Description of Contorograms in Fig. 2 and Fig. 3.

	Dry.	Sol. Oil.	Min. Oil.	Graph. Min. Oil.
Mild steel :				
Across machining marks . .	A	B	C	D
Along machining marks . .	E	F	G	H
Free-cutting steel :				
Across machining marks . .	I	J	K	L
Along machining marks . .	M	N	O	P



FIGS. 2 and 3.

If a contorogram be taken across a turned or bored surface, a contour such as *A* will be obtained. A contorogram along the direction of machining will be as at either *B* or *D*, depending on whether a smooth or rough action is taking place. To compute the degree of roughness, the total depth of roughness must be taken, but also the area that will come into contact as the surface is imagined to be worn away as indicated by, say, the middle horizontal line at *A*.

TABLE II.

		Dry.	Sol. Oil.	Min. Oil.	Graph Min. Oil.
Mild steel :					
Depth of roughness across machine marks		700	350	350	400
Depth of roughness along machine marks		300	300	200	150
Percentage bearing area across machining marks after the indicated depths of wear	100	2	5	20	25
	200	10	45	40	48
	300	35	75	80	95
	400	70	100	100	100
	500	95	100	100	100
Percentage bearing area along machining marks after the indicated depths of wear	100	34	35	70	80
	200	80	90	100	100
	300	100	100	100	100
	400	100	100	100	100
	500	100	100	100	100
Total percentage bearing area after the indicated depths of wear	100	0·68	1·75	14	20
	200	8	40	40	48
	300	35	75	80	95
	400	70	100	100	100
	500	95	100	100	100
Free-cutting steel :					
Depth of roughness across machine marks		450	350	250	325
Depth of roughness along machine marks		250	250	150	100
Percentage bearing area across machining marks after the indicated depths of wear	100	14	24	30	34
	200	37	63	62	60
	300	75	95	95	100
	400	98	100	100	100
	500	100	100	100	100
Percentage bearing area along machining marks after the indicated depths of wear	100	30	70	70	100
	200	80	95	100	100
	300	100	100	100	100
	400	100	100	100	100
	500	100	100	100	100
Total percentage bearing area after the indicated depths of wear	100	4·2	16·8	21	34
	200	29·6	60	62	90
	300	75	95	95	100
	400	98	100	100	100
	500	100	100	100	100

Note.—All depths in micro-inches.

If the surface has a contour across the machining marks as at *A*, and along the machining marks as at *B*, then *C* will indicate the bearing area after the wear indicated, whilst the bearing area will be as at *E* if the contour along the machining marks is as at *D*.

So the roughness in all directions must be considered. In the tests under consideration the criterion for smoothness is the total depth of roughness across and along the machining marks, and the total bearing area at different depths of wear.

Turning tests were made using Wimet tools at 1000 ft. per minute with a cut of $\frac{1}{32}$ in. and a feed of 270 per in. Figs. 2 and 3 are typical of the contorograms obtained.

Analysis of these contorograms and Table II will show that free-cutting steel has a better finish generally than mild steel; the roughness under dry conditions being 450 micro-ins. for the free-cutting and 700 micro-ins. for the mild steel. The average reduction in the depth of roughness due to the change to free-cutting steel is 23 per cent., whilst the bearing area is very considerably increased by amounts varying from an 800 per cent. increase in area to a 50 per cent. increase in area, depending on the cutting conditions. The change from cutting dry to a soluble oil reduces the depth of roughness by an average of 30 per cent.; the change from soluble to mineral oil reduces it by 25 per cent.

Examination of contorograms *D*, *H*, *L* and *P* will show that the colloidal graphite addition to the mineral oil does not reduce the depth of roughness across the machining marks, but does alter the nature of the shape, making it more regular, as shown by the even shape of the contours *D* and *L*. The colloidal graphite, on the other hand, very considerably reduces the roughness along the machining marks, as shown by the smoothness of *H* and *P*.

It is this greater smoothness along the machining marks that increases the bearing area given in Table II for the graphited mineral oil.

It is the roughness along the machining marks that is most greatly affected by any improvement in the cutting conditions. In the example under consideration, the colloidal graphite, by reducing the friction between the chip and the top of the tool, reduces the jerking action of the chip, which jerkiness no doubt causes considerable roughness on the work.

An ordinary cutting fluid or oil must form a liquid film between the tool and the chip to act as a lubricant, and it is very difficult for such a film to be maintained under the cutting action, particularly right at the cutting edge, where the temperature is such as to volatilize the lubricant. The colloidal graphite, on the other hand, can lubricate the top face of the tool without forming an actual liquid film, but by forming on the surface of the tool a graphoid film, and this film will stand heavy pressure without being destroyed, and moreover will lubricate at the high temperature * created at the extreme tool edge.

The influence of speed on the finish as shown in Fig. 4 shows that the finish improves with speed to a point, and then gets worse with increase in speed. The change-point occurs at about 800 ft. for high-speed steel cutting mild steel with soluble oil (*A*) and mineral oil (*B*). With graphited oil (*D*), or with free-cutting steel with soluble oil (*C*), the point is at about 1000 ft. With Wimet tools on mild steel the change-point is at about

* H. Higinbotham, Discussion on Lubricants, *J. Inst. Mech. Eng.*, **1**, p. 480.

1100 ft., whilst with Wimet tools on free-cutting steel the change-point is at 1300 ft.

It will be seen that when colloidal graphited oil is used, or a free-cutting steel is cut, or a Wimet tool used, the curve does not rise as steeply after the change-point, indicating that the cutting condition is not greatly worsening.

Figs. 1, 2 and 3 by courtesy of *Mechanical World*.

Mr. H. Higinbotham (E. G. Acheson, Ltd.) wrote: Reference has already been made by one of the authors to the tests carried out by Professor Boston at Michigan University, but it may not be out of place to note some of his findings as a result of tests made with colloidal graphited lubricants.

The effect of the addition of colloidal graphite to soluble oils using high-speed tool steel on nickel chrome steel with shallow cuts at low speeds was an appreciable increase in cutting speed and tool life. Boston indicates that the finish was equal in smoothness to that obtained by any of the oils tested. There is an indication here that the graphite was giving increased lubrication value to the emulsion, so that its usefulness was increased.

Boston's tests with a mineral oil containing colloidal graphite indicated much improved tool life and increase in cutting speed, and it is also stated by this authority that the finish produced by such a graphited oil was the best of all. Thus we see that, in addition to an increase in cutting speed and extension of tool life, there was a better finish obtained on the work.

It is possible that Boston's tests did not reproduce actual working conditions or conditions usually met with in this country, but the results do seem to give a clear indication of what one may expect to obtain under service conditions.

It is not difficult to see why there is a beneficial effect from the addition of colloidal graphite to cutting lubricants when one considers the lamellar structure of graphite. In this connection we refer to the paper by Professor Adam before the Institution of Mechanical Engineers' General Discussion on Lubrication and Lubricants, in which he points out:

> ". . . Graphite consists of plane sheets of carbon atoms, of indefinite and large extent, exceedingly tightly linked together in the sheets; each sheet is, however, rather loosely attached to the next sheet parallel to it, and sliding or separation can easily take place. It is known, from studies of electron diffraction, that graphite is easily attached to metal surfaces, these sheets being parallel to the surface; the sheets afford protection against seizure between the metals. When real contact occurs, it will be between the outside of the sheets of graphite and not between the metals. When separation occurs, the graphite is the weakest link in the bridge, and breakage occurs in the graphite and not in the metal. This tends to flake the graphite into tiny, flat particles, which will remain in the oil and be available for repairing any gaps accidentally formed in the layer of graphite covering the surface. Therefore, while graphite alone is valuable as a lubricant, the combination of graphite and oil is far better, for even apart from the lubricating power of the oil, which is, of course, considerable, the oil acts as a carrier of flakes of graphite to wherever they may be required, and thus tends to preserve the protecting covering."

Colloidal graphite also has the property of preserving its lubricating qualities at high temperatures, such as are met with in cutting operations. Additionally, it is inert, and therefore not likely to affect the metal surfaces nor the operators.

The use of lubricants containing colloidal graphite is not suggested for all cutting operations, but it is believed that in cases where finish of the work is of prime importance, then this type of lubricant should be of service.

It is the writer's suggestion that as the data on cutting lubricants are not very extensive, especially in the light of modern high-speed conditions, further extensive research work is desirable, and is believed to be contemplated.

Mr. A. L. Reed (Sternol, Ltd.) wrote: The papers by Professor Swift, Messrs. Lloyd & Beeny and Mr. Mason, deal adequately with the theoretical and practical requirements of cutting fluids, their functions, properties and selection from the user's point of view. Mr. Miller has, however, trespassed over the same ground, and, beyond indicating some of the commonly known ingredients of cutting oils, said nothing about their actual manufacture. I think, too, that it should be emphasized in this discussion that the formulæ given on p. 646 of Mr. Miller's paper have appeared in another publication, and that they do not in any way represent current British practice.

The drip-test developed in the Herbert Laboratory for assessing the corrosive tendencies of soluble oil emulsions is a valuable addition to laboratory technique, giving a fairly reliable indication of results which may be expected in the machine shop. The work done by Messrs. Lloyd and Beeny has led them to favour certain oils of the so-called clear type which yield transparent solutions in water; oils of the sulphonated fatty-oil type being corrosive under the conditions of this test due to their high free fatty-acid content. And yet large quantities of the sulphonated fatty-oil type of soluble oil are being used to-day with apparently satisfactory results. How can this anomalous position be explained? The transparent emulsions approach almost to true solutions, and are undoubtedly far more stable than the milky emulsions. A good transparent emulsion may be boiled until a large proportion of the water has evaporated and still remain clear (Messrs. Lloyd and Beeny express this point in their paper when speaking of the strengthening of the solution in use). In the emulsions we are considering we have soap solution as the continuous phase with mineral oil, and perhaps neutral fatty oil as the dispersed phase. Clear oils are used at much greater dilutions than are the sulphonated-oil type, and there is therefore more dispersed phase in emulsions of the latter, not only on account of dilution, but also of composition.

Hence, it would seem that where soluble oils of the sulphonated-oil type are being used satisfactorily, the results are achieved by their relative instability—a film of separated oil being deposited on the work, thus masking to some extent the deleterious effects of the high free fatty-acid content. Anyone who has watched this type of emulsion in use must agree that it is unstable, and this is further borne out by the fact that the emulsion actually becomes weaker in use, oil being separated and held back by the work and by filtration through the swarf.

On the contrary, the success of clear soluble oils would appear to be due to their greater stability and to the correct chemical condition of the continuous phase, one essential requirement being a p_H value of not less than 8·5.

Mr. C. B. Wingfield (Smith Brothers & Co.) wrote: I join with other members in thanking the authors of the papers for such an interesting evening, but feel that there are one or two points which need a little further explanation.

For example, Mr. Miller, in the third paragraph of the first page of his paper (p. 645), remarks:

> "Oils such as rape, sperm and lard have rendered a unique service to engineers for many decades, and although still preferred by some for lubricating heavy-duty broaching, tapping and screwing operations, they are now obsolete on the high-production machine tools where the heat generated is sufficient to break them down."

I presume that the "high-production machine tools" to which he refers are automatic or semi-automatic machines. If so, this does not agree with Mr. Beeny's views, whereby he states that the policy of Alfred Herbert, Ltd., is to recommend a neat cutting oil for all automatic and semi-automatic machines.

I am inclined to agree with Mr. Beeny, since my experience has been that the straight-cutting oils will stand up to greater temperatures and more severe cutting operations than soluble oil emulsion.

There is also another point where these authors disagree, and that is, Mr. Miller, whilst not actually condemning the new transparent or translucent soluble oil emulsions, does, however, state that they have service disadvantage of gumming up moving parts of the machine tool. On the other hand, we have Mr. Beeny claiming that these are the most superior types of emulsions he has tested, and highly recommending their use.

In this case, my experience definitely points that the transparent or translucent soluble oil emulsions are undoubtedly superior to the ordinary opaque type, inasmuch as they possess greater anti-rust properties, show no signs of gumming whatsoever, and can be used at greater dilutions.

Mr. J. F. Miller, in reply to the discussion, wrote as follows:

In reply to Mr. A. E. Lawson.

By "wetting the metal surface," reference is made to a physical property possessed in varying degrees by all liquids. An efficient "wetting" action reduces the interfacial tension between the metal and cutting oil, and so assists the rapid formation of the necessary film—that is to say, the oil spreads quickly. This point is also emphasized by Dr. Bowden with his reference to "speed of film formation." The process of "wetting" can be demonstrated by taking some cotton linters and dipping them in distilled water. The water does not readily penetrate the fibres. Then repeat the test with water containing 1 per cent. of soluble oil and the fibres are wetted immediately.

In reply to Mr. Romney.

One cannot have a true solution of mineral oil in water, and as mineral oil is present in all so-called clear soluble oils, what appears to be a solution is actually a finely dispersed emulsion.

On the question of gumming up of machines raised by Mr. Romney and Mr. C. B. Wingfield, the writer can only add that this has been his experience, having seen various machines in a badly gummed condition after using certain clear soluble oils.

In reply to Mr. C. B. Wingfield.

In connection with the mention of the use of rape, sperm and lard oils on high-production machines, it is not inferred that other straight oils are not suitable. The reverse is the case, and warm endorsement can be given to the use of neat oils such as sulphurized/mineral, lard/mineral and fatty/mineral oil blends on the machine tools mentioned.

On the question of dilutions, the author's experience is that soluble oils of the opaque type will stand greater dilutions than the clear type.

MESSRS. A. H. LLOYD and H. H. BEENY, in reply to the discussion, wrote :

Mr. Lawson's contribution to the discussion is interesting, and his statement that sulphur in cutting oils increases the load-carrying capacity will meet with general acceptance, but the significance he attributes to high sulphur in free-cutting steels has another explanation. Sulphur in properly made steels is in the form of manganese sulphide, which freezes before the parent metal and forms innumerable small globules, which are dispersed more or less evenly throughout the ingot. At rolling temperatures the pellets are plastic, and are consequently drawn out, so that they appear in the final bar as fine threads. These threads have no useful strength, and they break up the continuity of the metallic matrix, so that the metal becomes less tough and ductile, and the chips which are formed during machining break away more easily in front of the tool, and thus avoid any piling-up or tearing of the metal. Phosphorus which is completely in solid solution in the steel embrittles the metal, and consequently has a similar effect.

Mr. Read remarks that large quantities of milky or opaque types of emulsion are used with apparent satisfaction, although they contain sulphonated fatty oil and free fatty acid, and can be proved to cause corrosion. A reason for this state of affairs is that executives are frequently unaware of the insidious damage which is being done day by day to their machine tools by rusting and deep etching of the cast-iron and steel surfaces. It is the earnest desire of the authors to direct attention to this aspect of aqueous cutting fluids, which is frequently neglected, particularly as now improved forms of soluble oil exist which are non-corrosive and are suitable for high-quality lathes and other machine tools where a straight cutting oil is not necessary. From this point of view also the authors are pleased to have confirmation from Mr. Wingfield's experience in regard to the superior qualities of the new translucent or clear soluble oils. He finds, as we have found, that the emulsions from these oils are phenomenally stable and non-corrosive, whilst giving " no signs of gumming whatsoever." Mr. Miller's statement that such emulsions have the disadvantage of gumming-up moving parts of the machine tool must refer to some peculiar type, as in nearly three years of experience with a fluid of this nature on some hundreds of machines the authors have never had a single instance of any " gumming " tendency.

PROFESSOR H. W. SWIFT, in reply, wrote that for the most part contributors to the discussion had accepted his paper for what it was invited and intended to be—a brief and simplified summary of existing knowledge of the action of cutting fluids, directing attention to essentials and to directions in which further inquiry is needed. For that reason the illustrations of the tool in cut were, as Mr. Lawson pointed out, diagrammatic, simplified and mainly conventional. The fact that a tool in practice usually cuts on the side as well as the face naturally involved modified valve angles to give any derived effective cutting angle, but did not affect the basic principles of cutting. If, as Mr. Lawson considered, it was "an illusion to imagine any considerable fissure preceding the arrival of the tool," it was an optical illusion, for it could be seen and photographed.

Mr. Lawson also disagreed with the statement that "there is experimental evidence that a slightly sulphurized oil has better anti-frictional properties than other fluids for which data are available." Mr Lawson was entitled to disagree with the evidence if he discredited the results obtained in a number of separate investigations by Boston and his associates, but he was not entitled to dispute the statement that such evidence exists. The author, for his part, entirely agreed with Mr. Lawson's claims for the "extreme pressure" advantages of sulphur, and Boston's results showed that fatty content assisted the anti-frictional qualities of most cutting oils.

The author accepted Mr. Lawson's remarks regarding the advantages of a low-viscosity compounded mineral oil in the crush-forming of grinding-wheel profiles, but pointed out that this is not, in fact, a grinding operation, and adhered to his view that cooling, as distinct from lubrication, is the essential function of a cutting fluid in grinding operations.

MR. H. J. MASON, in reply, wrote:

Mr. A. E. Lawson refers to hobbing operations on water-soluble and straight oil cutting media, and he would be interested to know that our experience is that tool life is only 3·5 per cent. longer when using the latter type of oil. This was one of the reasons why in my paper I refer to the desirability of exploring the possibilities of water-soluble oils before using the more costly straight oils.

In reply to Mr. Romney regarding the laboratory placings of the five oils referred to in my paper, these oils were stated as straight cutting oils, and the laboratory checks referred mainly to emulsion-type oils. There was no attempt, therefore, to place an order of merit on the laboratory tests, since it is considered that the only real test is the practical one. I am sorry that Mr. Romney feels that we are unable to keep abreast with all modern developments in cutting oils, but I would like him to realize that the data on each type of oil under test were obtained after making some 8,000–10,000 components each, and that in one series of tests we handled some fourteen types of oil. Much as I would like to elaborate our test procedure, our results have shown that the effort required to undertake these fourteen examinations is as much as can be justified on that one subject.

Mr. G. H. Thornley feels that my rust test needs some refinement, but I find that when dealing with tests involving atmosphere control, they become unnecessarily complicated, and if a test such as I have outlined in my paper is performed on all samples at the same time, and therefore under the same conditions, at least strictly relative results are obtained.

TREATMENT OF SHALE OIL BY HYDROGENATION.*

By M. Pier.†

Summary.

The experiments described indicate that it is possible by catalytic hydrogenation under pressure to produce marketable products of high purity with exceptionally high yield from shale oil and from the oils obtained by low-temperature carbonization of shale.

Paraffin wax, lubricating oil and diesel oil can be obtained from Scottish and similar paraffinic shale oils with almost 100 per cent. yield by weight. The properties of the lubricating oils correspond to those of Pennsylvanian machine oil. Paraffinic and asphaltic shale oils, such as Estonian shale oil, can be converted with 85 per cent. yield by weight into diesel oil with cetene number 60–75, together with a small quantity of petrol.

All types of shale oil can be converted into motor petrols with approximately 80 per cent. yield by weight—*i.e.* more than 100 vol.-per cent. yield, which have octane numbers between 65 and 67 and possess a high lead sensitivity. Petrols of higher knock-rating may be produced by reduction of the end-point, and in particular by means of aromatization.

Bituminous and brown coal play an important part in the production of mineral-oil products in countries which are indigent in petroleum oils. In other countries oil shales possess a similar importance. If one is dependent on a purely thermal process—*i.e.* high- and low-temperature carbonization—for the production of oil from coal and shale, the yield and the properties of the final products are confined within fairly narrow limits, according to the nature of the raw material. Oil shales are similar both to coal and petroleum oils, and therefore similar methods are required for their processing. This holds true not only for thermal processes, but also in particular for high-pressure hydrogenation, which, in addition to other advantages, possesses an almost unlimited adaptability to the nature of the raw materials and the properties of the marketable finished products.

Catalytic high-pressure hydrogenation is already employed on a large scale with great success for the production of mineral-oil products from coal and tars. In the present meeting, devoted to the discussion of oil-shale processing, it may be of interest to investigate the possibilities which the application of hydrogenation to oil shales and shale oils offers, and how far this process may with advantage be used in conjunction with other processes.

Oil Shales, Shale Oils, Coal and Petroleum Oils.

As in the case of coal, oil shales contain inorganic material. In general, as with bituminous coal, the water content of oil shales does not exceed

* Paper presented for discussion at the Conference on Oil Shale and Cannel Coal, held in Glasgow, 6th–11th June, 1938.

† Together with co-workers Department "Hochdruckversuche" of the I.G. Farbenindustrie A.-G., Ludwigshafen-Oppau.

20 per cent., whereas up to 60 per cent. moisture may be present in brown coal. Shales usually contain more ash than coal. The ash content of shales varies between 20 and 75 per cent. or more, whilst in the case of bituminous coal it varies between 4 and 12 per cent., and in the case of brown coal between 5 and 15 per cent. With bituminous coal a considerable reduction in inorganic content may be achieved by purely mechanical means, since a large part of the ash consists of gangue. As a large portion of the

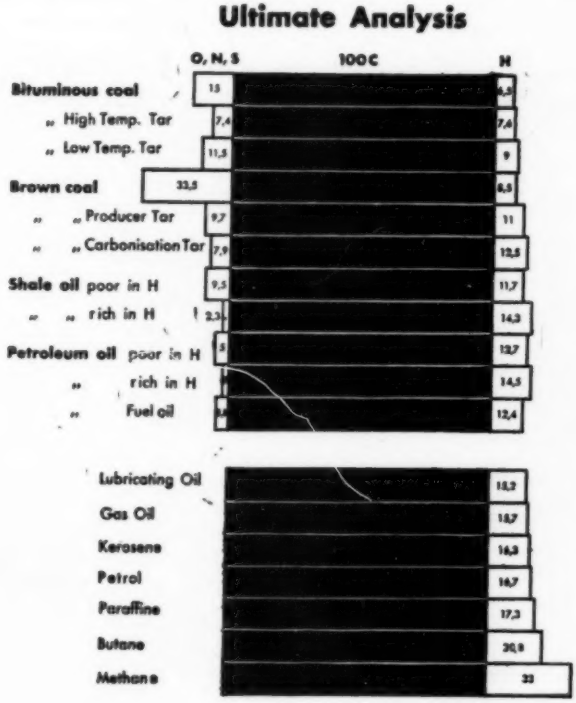


FIG. 1.

ash in brown coal is present in chemical combination with organic material, chemical methods of concentrating the organic matter must be applied—as, for example, treatment with mineral acids. Mechanical separation is impossible in the case of shale, and chemical separation has also little hope of success.

The C : H ratio in the organic material in shale—about 11–14 H/100 C—corresponds more closely to that of petroleum oils with about 12–14 H/100 C than to that of coal, since brown coal, for example, contains 7–9 H/100 C. Moreover, in some shale deposits the organic material contains as much oxygen as coal. Oil shales resemble bituminous coal

in that the organic material cannot be extracted in normal circumstances with ordinary organic solvents, whilst from brown coal a portion of the organic matter, especially bitumen and resinous material, may be extracted at atmospheric pressure. As in the case of coal, by extraction at high temperature and pressure a large portion of the organic material in the oil shale can be brought into solution with slight depolymerization. Both coal and shale when subjected to heat-treatment yield low-temperature carbonization products by decomposition of the organic material. Based on the organic matter, the yields obtained from shale are higher than from coal, so that shale in this respect takes up an intermediate position between coal and petroleum oil.

Oils obtained by the destructive distillation of shale resemble partly petroleum oil and partly coal tars, as the following two tables and the graph show:

Paraffinic Shale Oil and Mixed-base Petroleum Oil.

	Paraffinic Shale Oil.	Mixed-base Petroleum Oil.
Total oil:		
Sp. gr. at 15° C.	0·882	0·906
Asphalt, %	0·35	0·31
Paraffin wax, %	9·3	3·7
Middle oil,* 180–325° C.:		
% of total oil	42·2	23·8
Sp. gr. at 15° C.	0·840	0·840
Residue above 325° C.:		
% of total oil	53·6	71
Sp. gr. at 50° C.	0·895	0·913
Residue above 325° C. at 12 mm., %	20·2	41·8
Ultimate analysis of total oil:		
C, %	85·81	86·08
H, %	12·29	12·26
O, %	0·26	0·87
N, %	1·32	0·25
S, %	0·32	0·60
H/100 C	14·3	14·2
H disp.	13·9	13·96

* The small quantities of petrol contained in the oils are omitted in this and the following table, as they were considered to be unimportant.

As a typical example of paraffinic shale oil, Scottish shale oil, which resembles very closely the oils from Australian, Fushun shale, etc., and mixed-base crude oil was chosen for the table. This resemblance is particularly evident from the asphalt content and the properties of the various fractions. As shale oil is obtained by destructive distillation, it contains less vacuum-residue and more middle oil than crude oil. The great similarity of the oils compared is also clearly evident from the ultimate analysis.

A similar good agreement between asphalt-base petroleum oil and asphaltic shale oil does not exist. On the other hand, asphaltic shale

oils—such as those, for example, obtained from Estonian shales—resemble closely in their properties certain coal tars.

Asphaltic Shale Oil, Brown-coal Tars and Asphalt-base Petroleum Oils.

	Asphaltic Shale Oil (Estonian).	Tar from Brown Coal rich in Bitumen.	Tar from Brown Coal rich in Oxygen.	Asphalt-base Petroleum Oil.
Total oil :				
Sp. gr. at 15° C.	1·006	0·951	1·033	0·910
Asphalt, %	6·7	1·2	8·2	2·1
Paraffin, %	0·01	11	9·5	0
Middle oil, 180–325° C. :				
Total oil, %	28·6	40·1	28·6	24·2
Phenols, %	19	21·8	24·4	0·28
Middle oil, dephenolated :				
Sp. gr. at 15° C.	0·883	0·908	0·930	0·856
Residue above 325° C. :				
Total oil, %	69·0	59·8	71·4	73·9
Sp. gr. at 50° C.	1·031	0·948	1·025	0·980
Residue above 325° C. at 12 mm., %	34	11·8	*ca.* 35	70
Ultimate analysis of total oil :				
C, %	82·45	83·42	82·60	84·72
H, %	9·62	10·55	9·24	11·71
O, %	6·00	4·09	7·64	1·88
N, %	1·07	0·17	0·29	0·21
S, %	0·86	1·75	0·23	1·48
H/100 C	11·68	12·67	11·19	13·83
H disp.	10·43	11·80	9·92	13·39

Examination of the analytical data shows that the above-mentioned Estonian shale oil takes up an intermediate position between tar from brown coal rich in bitumen and tar from brown coal rich in oxygen. Particularly striking is the good agreement in the ultimate analyses. A certain deviation is evident in the case of the dephenolated middle oil, the density of which is lower than in the case of brown-coal-tar middle-oil. The absence of paraffin in asphaltic shale oils does not correspond to brown-coal tar, but shows a resemblance to bituminous coal low-temperature tar, which seldom contains more than 0·1 per cent. paraffin. It may be mentioned that bituminous-coal low-temperature tars have not been brought into the comparison, as the hydrogen content is considerably lower than that of shale oils. From these observations we may deduce the basic principles for the processing of shales and shale oils.

Processing of Shale Oils.

For the recovery of oil shale the organic material must be separated from the ash as far as possible. Up to the present this has been carried out exclusively by low-temperature carbonization. The properties of the products obtained and the yields are dependent both on the carbonization process and on the nature of the shale. For example, oil yields of only about 5–6 per cent. by weight are obtained from rock with low oil content,

such as are found in Germany, Sweden and Italy. Fushun shale, which is technically processed, gives also a similar small oil yield. Scotch oil shales yield about 8–10 per cent. oil, Estonian shale up to 30 per cent. and Australian up to 45 per cent. In general, the oil yields obtained by carbonization on a technical scale do not greatly exceed two-thirds of the organic material contained in the shale. Carbonization of the same shales in the laboratory gives a somewhat higher yield. The endeavours of the shale-oil industry naturally aim at an increase in the yield by improvement of the carbonization methods—for example, by different types of carbonization with carrier-gas, and by alteration in the construction of the retorts.

It is also necessary to investigate whether, apart from carbonization, other processes are suitable for the recovery of the oil contained in shale. Up to the present no success has been obtained in the de-ashing of shale by the methods used for coal—for example, application of the swim-sink process or acid treatment. There remains, however, the possibility of separating the ash from the organic matter by extraction with organic solvents. Extraction at atmospheric pressure results in only a very small amount of the organic matter being brought into solution. It is easy, however, to extract more oil from shale by the application of pressure, high temperature and suitable solvents than can be obtained by carbonization. For example, a sample of Estonian shale which gave on carbonization in a Fischer aluminium retort 53 per cent. oil on the organic matter, yielded by extraction with a bituminous coal-tar oil at 80 atm. pressure and at the relatively low temperature of 410° C., 67 per cent. of extract on the organic matter. As a result of the low extraction temperature the original high-molecular structure of the organic matter in the shale is only slightly broken down, so that the extract consists of a high-boiling product containing about 25 per cent. asphalt.

The extraction can also be carried out with other solvents, as, for example, with those which have been successfully employed for the extraction of coal. In order to convert the ash-free, high-molecular extract into marketable products with high yield, it must be further treated by hydrogenation as in the case of high-molecular petroleum oil or coal extract.

Instead of employing extraction followed by hydrogenation, higher oil yields than those obtained by carbonization may be achieved by the direct hydrogenation of oil shale. A practically complete conversion of the organic material present in the oil shale may be obtained by hydrogenation, which is the normal method employed to convert coal as completely as possible into petrol, diesel oil, etc. In some cases carbonization followed by hydrogenation of the tar is chosen when, in addition to a high tar yield, there exists an economic outlet for the coke, which frequently in quality and value is the chief product. In the case of oil-shale hydrogenation the conditions are somewhat different, in that the oil shale gives in general a higher yield on the organic material than coal on carbonization, and the value of the residue is of less importance, due to its high ash content.

Hydrogenation of oil shale may be carried out in the same way as coal, the shale being pasted with heavy oil and subjected to hydrogenation under the same conditions of temperature, pressure and catalysis. In the first stage—the so-called liquid phase—a practically complete conversion of the organic matter was obtained in preliminary experiments

with Australian and Estonian shales. It is possible in the first stage to produce heavy oil, middle oil and petrol, but it is also possible to carry out the reaction in such a manner that only middle oil and petrol are produced. Compared with coal hydrogenation, oil shale possesses the disadvantage that large quantities of ash must be conducted through the high-pressure reaction space and subsequently separated from the oil. On the other hand, the comparatively low consumption of hydrogen is a decided advantage.

In order to form a picture of the type of product obtained from shale, some preliminary experiments were carried out in which shale was hydrogenated without pasting oil. As was to be expected from corresponding experiences in the hydrogenation of coal, a product was obtained with practically the same properties as a carbonization product from the same shale, the only difference being that the product of hydrogenation was somewhat lower in oxygen content.

The process for the direct recovery of oil from shale by hydrogenation or extraction would only be further developed technically if it proved to possess advantages compared with carbonization.

Shale-oil Hydrogenation.

As shale oils are not basically different from coal tars and heavy petroleum-oil products, the process of high-pressure hydrogenation which has already been fully developed and successfully used on a large scale can be employed without alteration. Catalytic high-pressure hydrogenation presents the most suitable method of treatment, with regard to economization in raw materials and with respect to the properties of the final products. This process can be employed alone or in conjunction with distillation, cracking or separation with selective solvents. The adaptability of hydrogenation to a very wide range of raw materials and the control of the properties of the desired final products are made possible by the fact that pressures up to 700 atm. or more can be employed on a large scale, and the reaction can be influenced to a large extent by suitable catalysts, temperatures and other conditions.

The present method of working up oil-shale products by distillation and refining produces marketable mineral-oil products, but only in quantities which correspond to those present in the crude product, as in the case of brown coal and bituminous coal tars. Cracking also results in lower yields than hydrogenation, especially in the case of oxygen-containing shale oils. In particular, it must be pointed out that the losses in cracking, which are often very considerable, may be avoided by the use of hydrogenation, and the latter process may be employed with success where other methods of refining have up to now failed—as, for example, with oils of very high sulphur content.

Liquid-phase Hydrogenation.

In the case of heavy oils, catalytic hydrogenation is applied in the liquid phase, whilst for light oils the vapour phase is used. For this purpose the

oils must first be fractionated by distillation. Oils of high asphalt content or distillation residues are generally converted into middle oils in the presence of finely-divided catalysts. In the vapour phase in which middle oil may be converted into petrol the reaction is carried out over fixed catalysts. In hydrogenation with finely-divided catalyst the concentration of catalyst is in general not high. The products may contain varying amounts of oxygen-, nitrogen-, sulphur- and also possibly unsaturated compounds, according to the nature of the feed. It is possible to change to a large extent the boiling range and asphalt content of the final products by suitable alteration of the reaction conditions, but the remaining properties can be influenced to a comparatively slight degree only.

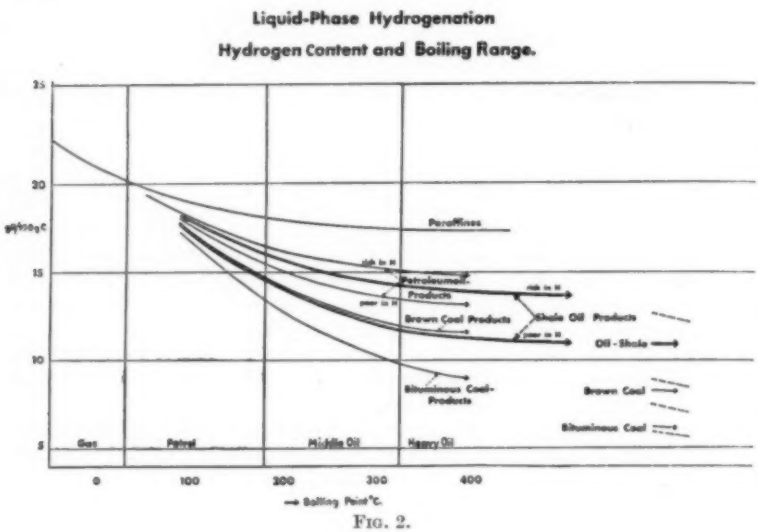


FIG. 2.

Fig. 2 shows the alteration of the hydrogen content when high-boiling products are converted into those of low-boiling range.

In the above diagram the hydrogen content and boiling range of various liquid-phase products are given, together with two types of shale oil. It can be seen that the hydrogenation of low-hydrogen-content paraffinic shale oil yields products which resemble oils from mixed-base petroleum oils, whilst the products obtained from low-hydrogen-content asphaltic shale oils resemble those from brown coal with respect to hydrogen content.

Continuous experiments have shown that by hydrogenation of heavy oil from shale oil in the liquid phase with finely-divided catalyst a satisfactory conversion into middle oil and of asphalts to oil is obtained. In the following table some data are given which were obtained by the hydrogenation of distillation residue from paraffinic and asphaltic shale oil.

Hydrogenation of Shale Oil Residues in the Liquid Phase with Finely Divided Catalyst.

Distillation Residue above 350° C. from Shale Oil.	Paraffinic (rich in H).	Asphaltic (poor in H).
Sp. gr. at 15° C.	0·919	1·060
Asphalt, %	0·55	16·5
Paraffin, %	17·4	0·02
Ultimate analysis :		
C, %	85·9	83·8
H, %	11·8	9·1
O, %	0·8	5·8
N, %	1·2	0·6
S, %	0·3	0·7
Yield in liquid phase hydrogenation :		
Weight % yield (middle oil and petrol) on the distillation residue	91	88
Vol. % yield (middle oil and petrol) on the distillation residue	99	105
Petrol in the product, %	11·0	19·6

With regard to hydrogen and asphalt content, the distillation residues differ widely, but on hydrogenation in the liquid phase they give practically the same high yields by weight of middle oil and petrol; in addition, gaseous hydrocarbons and some water, hydrogen sulphide and ammonia are formed. The difference in the two raw materials is chiefly shown in the properties of the products. As the following table indicates, the specific gravity of the middle oil from the paraffinic oil shale is lower than that from the asphaltic oil shale. The aniline point and the cetene number are correspondingly higher and the content of unsaturateds is lower.

Distillation and Liquid-phase Middle Oils from Shale Oils.

Middle Oil from Shale Oil.	Paraffinic (Rich in Hydrogen).		Asphaltic (Poor in Hydrogen).	
Method of Production.	Distillation.	Hydrogenation in Liquid Phase.	Distillation.	Hydrogenation in Liquid Phase.
Middle oil :				
Sp. gr.	0·840	0·858	0·938	0·914
Phenol, %	1·2	—	19·0	13·8
Middle oil free of phenol :				
Sp. gr.	0·833	0·858	0·907	0·894
Aniline point, ° C.	54	61	8	20
I.B.P., ° C.	195	220	201	196
–200° C., %	1·4	—	—	—
–225° C., %	22	2·9	10·1	11·1
–250° C., %	42·6	20·4	27·2	28·0
–300° C., %	86·6	58·2	62·2	61·1
–325° C., %	96·6	79·0	78·0	78·5
–350° C., %	330	97·0	89·4	90·2
Cetene number	57·0	57·0	39·5	41·5
Pour point, ° C.	—	—	–38	–31
Olefines, %	13·0	11·0	35	22

In addition, the table supplies a comparison between the middle oils obtained by liquid-phase hydrogenation of the residue with that obtained by distillation of the crude shale oil. It shows that the liquid-phase middle oils very much resemble the distillation middle oils. There exist some small differences. For example, liquid-phase middle oils contain less unsaturateds and phenols. Liquid-phase middle oil from asphaltic shale oil has a higher hydrogen content than the middle oil obtained by distillation. In the case of paraffinic shale oil this difference is not so marked. The middle oil from paraffinic shale oil can be employed without further treatment as diesel oil, whilst with asphaltic shale removal of phenols is advisable. Phenol removal may be carried out with advantage by hydrogenation over fixed catalyst, since by this means an improvement in the cetene number and saturation of the olefines, which are present in a comparatively high concentration, is achieved.

Vapour-phase Hydrogenation.

Oils of medium boiling range obtained from distillation of the crude oil or liquid-phase products (E.P. about 325–350° C.) are treated over fixed catalyst in the so-called vapour phase. The reaction can be so controlled that the middle oils are subjected to a refining hydrogenation without substantial splitting, or they may at the same time be split to petrol.

In refining hydrogenation the phenols are reduced, the unsaturated compounds saturated and the sulphur and nitrogen removed. As splitting of hydrocarbon compounds takes place to a slight degree only, practically no formation of gaseous hydrocarbons results. Losses in weight are caused merely by the formation of water, hydrogen sulphide and ammonia. The middle oils in the product are water-white, light stable oils, which can be utilized as diesel oils or, if required, as kerosine. The character of the raw material is still recognizable to a certain extent, but becomes more and more indistinct as the degree of hydrogenation is increased.

When middle oil is split, gaseous hydrocarbons are formed in addition to petrol. In order to reduce their quantity as far as possible, the conversion to middle oil is not carried out completely in one stage, unconverted middle oil being again conducted together with fresh feed over the catalyst. The petrol distilled off from the product is stabilized and apart from a slight caustic wash requires no further refining. These petrols thus obtained correspond in their boiling characteristics and degree of purity to the usual market specifications. With regard to their performance in motors—*i.e.*, octane numbers—differences arise according to the raw materials employed. By use of various catalysts and hydrogenation conditions the petrols can be made to comply with all possible requirements. Without basic change in operating conditions, motor spirit and low end-point petrol can be produced, the latter suitable for aero-engines.

For the production of petrol and diesel fuel in the vapour phase both the middle oil obtained by distillation of crude shale oil as well as the middle oil from the hydrogenation of the higher-boiling fractions in the liquid phase can be used.

In the following table the properties of a mixture of these middle oils

obtained by distillation and hydrogenation are shown for asphaltic and paraffinic shale oils respectively.

Middle Oils Obtained by Distillation and Hydrogenation of Shale Oil.

Feed Stock.*	Asphaltic Shale Oil Poor in Hydrogen.		Paraffinic Shale Oil Rich in Hydrogen.
Sp. gr.	0·923		0·847
Aniline point, ° C.	+14 (dephenolated)		+56
Phenols, %	16		0·8
Boiling range : I.B.P., ° C.	196		195
–200° C., %	2		1
–225° C., %	11		16
–250° C., %	28		32
–300° C., %	61		78
–325° C., %	78		91
–350° C., %	90		—
E.P., ° C.	358		345
Hydrogenation Products :	**With Mildly Hydrogenating Catalyst.**	**With Strongly Hydrogenating Catalyst.**	**With Mildly Hydrogenating Catalyst.**
Sp. gr.	0·856	0·810	0·804
Aniline point, ° C.	53	69	75
Phenols, %	0·1	0·03	0·02
Boiling range : I.B.P., ° C.	201	200	198
–200° C., %	0	0	0
–225° C., %	19	19	19
–250° C., %	45	49	50
–300° C., %	84	91	90
–325° C., %	93	96	97
E.P., ° C.	348	330	330
Cetene number	55	70	76
Pour point, ° C.	−32	−38	−13
Olefines, %	1	0	0

* Mixture of distillation- and liquid-phase middle oil.

The properties of two types of middle oil are given in the table, one being obtained from asphaltic, the other from paraffinic shale oil. Apart from the hydrogen content the two oils differ widely in phenol content.

When these middle oils are refined by hydrogenation nearly 15–20 per cent. by weight boiling below 200° C. and 80–85 per cent. middle oils are formed, the properties of these oils being given in the same table. Even with a mildly hydrogenating catalyst a middle oil poor in hydrogen—for example, Estonian shale oil—yields a good diesel oil, which is practically free from phenols and has a cetene number of 55. As is to be expected from the low paraffin wax content of the shale oil, the pour point is exceptionally good (− 32° C.). Under the same conditions a diesel oil may be produced from middle oil of high hydrogen content—for example, Scottish shale oil, which possesses the very high cetene number of 76. Diesel oils with approximately the same satisfactory ignition characteristics may also be produced from low-hydrogen-content middle oil by the use of strongly hydrogenating catalysts. Compared with diesel oil from paraffinic middle oil such oils possess the advantage of a lower pour point.

Petrols obtained by treatment of shale oil middle oil under conditions of destructive hydrogenation comply with the tests and boiling-range characteristics of the best market products. They contain about 1–1·5 per cent. unsaturated compounds, and their gum content is only 2–3 mg./100 c.c. petrol. The sulphur content lies below 0·01 per cent.

It may be seen from the following table that the differences in the raw materials show up in the properties of the petrols, although to a less extent than in the case of diesel oils.

Petrols Obtained by Hydrogenation of Shale Oils.

Petrol from :	Estonian Shale Oil.	Scottish Shale Oil.
Sp. gr.	0·732	0·712
Aniline point, ° C.	50	59
−70° C., %	18	18
−100° C., %	42	42·5
−150° C., %	81	81·5
E.P., ° C.	185	187
Paraffins, %	58·5	75·5
Naphthenes, %	31·5	18·5
Aromatics, %	9	5
Unsaturateds, %	1	1·0
Octane number (C.F.R.-motor method)	66	65
+ 0·09 vol.-% lead tetraethyl	83	84

Paraffinic shale oil yields a petrol with a high content of paraffinic hydrocarbons which are partly present in the form of *iso*paraffins. On the other hand, the petrol produced from shale oil of low hydrogen content contains less paraffin and correspondingly more naphthenic and aromatic components. These differences are less evident in the knock-rating behaviour, whilst the lead sensitivity is, as in the case of all hydrogenation petrols, good.

If the petrols are cut to a low end-point the knock-rating characteristics are substantially improved. For example, it is possible to produce from a high-hydrogen-content shale oil a petrol, end-point 150° C. and 58 per cent. −100° C., which possesses an octane number of 69·5 and a vapour pressure of 0·49 at 38° C., and which has an octane number of 88·5 after the addition of 0·09 per cent. of lead tetraethyl.

Moreover, it is possible, by choice of catalysts, temperature, oil partial pressure and total pressure, to influence the properties of the petrol. In the following table, based on experiments carried out at Ludwigshafen, is indicated how by change of catalyst at the same operating temperature the properties of the petrol—in particular the knock-rating—may be varied.

By use of the strongly hydrogenating catalyst A a petrol is obtained from shale oil rich in hydrogen which possesses an octane number of 54. By use of the mildly hydrogenating catalysts B and C the octane number can be increased to 65 and finally to 67 without loss in yield. Under these conditions the petrol could be cut to an even higher end-point, which would naturally lead to an increase in yield. In the cases considered the yields are 91–92 weight per cent. or 107–108 vol. per cent. on the middle oil converted. For the production of the petrols B and C two catalysts are

employed, the one serving for non-splitting and the other for splitting hydrogenation.

Petrols Obtained from Scottish Shale Oil with Different Catalysts.

Catalyst :	A.	B.	C.
Petrol :			
Sp. gr.	0·712	0·712	0·722
Aniline point, ° C.	58·5	59	57
−70° C., %	17	18	17
−100° C., %	40·5	42·5	40
−150° C., %	89·8	81·5	82
E.P., ° C.	168	187	187
Octane number (C.F.R.-motor method)	54	65	67
+ 0·09 vol.-% lead tetraethyl	75	84	84·5

By use of higher working temperatures and catalysts suitable for aromatization conditions, it is possible to produce petrols with even higher octane numbers. From middle oil corresponding in chemical behaviour to the middle oils obtained from asphaltic shale oils, a petrol with octane number 77 (C.F.R.-motor method) was produced by aromatization with a yield of approximately 80 vol. per cent.

Hydrogenation of Total Shale Oil over Fixed Catalyst.

It has been shown above how shale oils may be converted into marketable diesel oils or petrol by hydrogenation in two stages : in the liquid phase with finely divided catalyst and in the vapour phase with fixed catalyst. It has further been pointed out that petrol and middle oil may be refined or hydrogenated over fixed catalyst at low temperature with little or no splitting. In the same manner low-temperature-carbonization tars from coal are converted over fixed catalyst without substantial alteration in the boiling range and with practically no gas formation. In our experiments Scottish shale oil was treated under these conditions, and a high-quality gas oil was obtained together with spindle oil, machine oil and paraffin.

As examples some data are given in the following table which show that mainly hydrogenation and saturation occurs.

Direct Hydrogenation of Shale Oil over Fixed Catalyst.

	Paraffinic Shale Oil.	
	Feed.	Hydrogenation Product.
Sp. gr. at 15° C.	0·891	0·857
Asphalt, %	0·35	0
Colour	dark	light yellow
Boiling range :		
−180° C., weight-%	0	0·6
180–325° C., ,,	30·2	34·8
above 325° C., ,,	69·8	64·6

The almost complete absence of splitting can be observed from the slight alteration in the boiling range, whilst at the same time the specific gravity is considerably lowered and the asphalts are completely reduced. The hydrogenation product obtained in a yield of 97 per cent. by weight was distilled and the high-boiling fractions dewaxed. The chief product was gas oil, with a yield of 65·4 per cent. by weight and, in addition to this, 17 per cent. by weight of machine oil, 17 per cent. by weight of paraffin and 0·6 per cent. by weight of petrol were obtained. The total gas oil (I) was fractionated into a low-boiling gas oil (II) and a spindle oil.

The analyses of the gas oils are contained in the following table :

Gas Oil.	I.	II.	Market Oil for Comparison.
Sp. gr.	0·856	0·838	0·848
Aniline point, ° C.	72·5	70·5	71
Boiling range : I.B.P., ° C.	190	190	215
–250° C., %	8·2	20·7	16·0
–300° C., %	29·8	61·6	59·7
–325° C., %	45·8	82·9	78·3
–350° C., %	62·6	93·3	91·2
End-point, ° C./%	360/70·9	360/96·3	360/97·0
Cetene number	68	67	60·5
Pour point, ° C.	–11	–18	–24
Sulphur, %	0·04	0·03	0·26
Viscosity, ° E./20° C.	1·58	1·21	1·20

With regard to specific gravity and boiling range, the gas oils correspond to normal market oils, but are superior to them in respect to the exceptionally good cetene number of 67–68. The extraordinarily low sulphur content of the hydrogenation gas oil is worthy of mention. The pour point of hydrogenation gas oils can be improved by lower cutting or by dewaxing.

When the gas oil II was distilled from the total gas oil I, a residual spindle oil remained, the properties of which are given in the following table. The spindle oil obtained from shale oil is at least equal, if not superior to good market oil, since it possesses a better viscosity index, a higher flash point and a lower iodine number.

Spindle Oil.	From Shale Oil.	Market Oil for Comparison.
Sp. gr. at 15° C.	0·874	0·897
Viscosity, ° E./20° C.	4·7	4·7
,, ° E./50° C.	1·83	1·79
Pour point, ° C.	–11	–10
Flash point, ° C.	186	154
Iodine number	14	24

The fraction of the hydrogenation product boiling above the spindle-oil fraction provides a machine oil, the properties of which are shown in the following table :

Machine Oil.	From Shale Oil.	Market Oil for Comparison (Pennsylvanian).
Sp. gr.	0·897	0·877
Viscosity, ° E./38° C.	7·5	8·5
,, ° E./50° C.	4·4	4·9
,, ° E./99° C.	1·6	1·65
Viscosity index	98	98
Pour point, ° C.	−11	− 2
Flash point, ° C.	225	220
Iodine number	17	20
Conradson test	0·11	0·30

With regard to viscosity index, the machine oil obtained from shale oil is equal to Pennsylvanian oil, and with respect to pour point, flash point and Conradson test it is even somewhat superior. The paraffin wax resulting from the dewaxing of the hydrogenation product consists of one-third hard and two-thirds soft paraffin, the melting points being approximately 53° and 35° C. respectively. In the experiments mentioned both

Petrol Production from Gas Oil Produced by Hydrogenation of Shale Oil over Fixed Catalyst.

Petrol with E.P.	185° C.	152° C.
Sp. gr.	0·726	0·721
Boiling range :		
−70° C., %	15·0	14·5
−100° C., %	41·0	52·2
−150° C., %	86·0	96·5
Vapour pressure at 38° C.	0·62	0·47
Octane number (C.F.R.-motor method)	67	71
+ 0·09 vol.-% lead tetraethyl	84	87·5
Gum, mgr./100 c.c.	3·0	2·0
Olefines, %	1·0	1·0
Aromatics, %	7·0	5·0

paraffins still contain oil, and in the case of the soft paraffin a considerable increase in melting point could be achieved by means of a sweating or similar process.

The gas oil produced by hydrogenation over fixed catalyst is suitable for the production of petrol by treatment with strongly splitting catalysts. In this manner the petrol given in the first column of the foregoing table was obtained with a weight yield of 92·5 per cent., having satisfactory tests and a high lead sensitivity.

If the petrol is cut to an end-point of 152° C. it possesses an octane number of 71, which can be increased by addition of 0·09 vol. per cent. lead tetraethyl to 87·5.

CHAIRMAN OF THE CHEMICAL STANDARDIZATION COMMITTEE

PROFESSOR J. S. S. BRAME

IT is with very great regret that the Council accepts the resignation of Professor Brame as Chairman of the Chemical Standardization Committee. He has been closely associated with the Institute's work on the standardization of methods of testing petroleum since its inception in 1922, and assumed the Chair of the Committee in 1929. He has seen the Committee grow from very modest beginnings to the authoritative position it occupies to-day. Under him have served over thirty sub-Committees and Panels dealing with every aspect of the problem.

Nobody knows better than his colleagues how valiantly Professor Brame has striven to render the publications of the Committee of real value to the petroleum industry. That he has succeeded is shown by the repeated editions of the Standard tests and their increasing significance.

Professor Brame has been able to keep together a very large team of collaborators, not only by his intimate knowledge of testing, but also by that characteristic geniality and kindliness, without which no great work is ever done.

The thanks of the whole body of members are due to Professor Brame for his work in the past, and we hope for his advice for many years to come.

A. E. D.

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